ALLEN'S
COMMERCIAL ORGANIC ANALYSIS

FOURTH EDITION REWRITTEN AND REVISED

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THE AMERICAN ELECTRO-CHEMICAL SOCIETY; MEMBER AMERICAN
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IN many respects this edition of Allen is a new work. The field of Commercial
Organic Analysis has been so enlarged and specialised during the last few years
that it has been found necessary to rewrite many parts and add much new matter.
Obsolete methods are omitted; what little of the old text remains has been care-
fully revised and many new illustrations added.

To accomplish the object in view, namely, the furnishing of a modern work
of the greatest practical value to the analyst, it was deemed advisable to secure
the services of an English and an American editor and to organise a corps of
writers particularly versed in the subjects discussed.

The general arrangement of the volumes remains as before, only such changes
have been made as will bring the text into line with the latest scientific classi-
fication. Great care has been exercised by the editors and contributors in the
choice of methods and only those of the highest degree of accuracy and rapidity
selected. Effort has been made to secure uniformity in weights and measures,
nomenclature and abbreviations. References are to original sources, not to
translations or abstracts.

The work is issued in nine volumes, numbered consecutively, as follows:

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ALLEN'S COMMERCIAL
ORGANIC ANALYSIS

A TREATISE ON

THE PROPERTIES, MODES OF ASSAYING, AND PROXIMATE ANALYTICAL EXAMINATION OF THE VARIOUS ORGANIC CHEMICALS AND PRODUCTS EMPLOYED IN THE ARTS, MANU-FACTURES, MEDICINE, Etc.

WITH CONCISE METHODS FOR

THE DETECTION AND ESTIMATION OF THEIR IMPURITIES, ADULTERATIONS, AND PRODUCTS OF DECOMPOSITION

VOLUME III

Hydrocarbons, Bitumens, Naphthalene and its Derivatives, Anthracene and its Associates, Phenols, Aromatic Acids, Gallic Acid and its Allies, Phthalic Acid and the Phthaleins, Modern Explosives

BY THE EDITORS AND THE FOLLOWING CONTRIBUTORS

F. C. GARRETT   EDWARD HORTON
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FOURTH EDITION. ENTIRELY REWRITTEN

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PREFACE.

In the present volume are included three distinct subjects: Bitumens, (including Aromatic Hydrocarbons and Phenols), Aromatic Acids, and Explosives. The last-mentioned article would have been perhaps more in place had it followed Cellulose or Glycerin. When one considers, however, the fact that all tests under the heading of Explosives are utterly distinct from those of Cellulose or Glycerin, the convenience in book-making in this case may be allowed to take precedence.

The editors desire to acknowledge their indebtedness to Mr. F. E. Dodge, formerly of Philadelphia, now residing in Chicago; to Mr. Edwin M. Chance, chemist of the Reading Coal and Iron Company, Pottsville, Pa., and to Mr. C. C. Tutweiler, chemist of the United Gas Improvement Company, Philadelphia, for their kind assistance in matters pertaining to pitch tests, creosote oils, and gas tars, respectively.

Considerable matter pertaining to asphalt specifications and tests is taken from the publications of Mr. Clifford Richardson, of the New York Testing Laboratories, New York City. These are quoted quite at length, as the exact adherence to these tests (as in many other instances) is absolutely necessary to obtain uniform results.

In accordance with the carefully prepared plan for the series, all parts of the book have been revised by those whose practical experience qualifies them to speak with authority.

Dr. Leffmann has found it impossible, owing to the pressure of many outside matters, to continue as American editor of the series and at the same time prepare those articles for which he has become responsible. His editorial work will, therefore, in the future be assumed by Mr. Samuel S. Sadtler, of Philadelphia.

The same system of abbreviation has been followed in this volume as in the preceding ones and is largely self-explanatory. In some places reference is made to solutions of the United States Pharma-

copœia. V. S. means volumetric solution, and in most cases is tenth-normal (N/10). T. S. means test solution. These solutions are of about the same strength as ordinarily used in chemical laboratories. The chief point at issue is that the chemicals should be of Pharma-copœial purity. Manufacturers of chemicals to be used as reagents are taking considerable pains to furnish very reliable articles, so-called "analysed chemicals."

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A. Marshall.

HYDROCARBONS.

By F. C. GARRETT, D. Sc.

The hydrocarbons (*i. e.*, those compounds which contain only carbon and hydrogen) fall into two great classes:

A. *The Aliphatic or Acyclic Hydrocarbons* (the paraffins, acetylene, etc.) in which the carbon atoms are linked together in open chains.

B. *The Cyclic Hydrocarbons* (benzene, naphthalene, etc.) in which some or all of the carbon atoms form a closed chain or ring.

THE ALIPHATIC HYDROCARBONS.

This large class is subdivided into several groups, according to the ratio between the numbers of carbon and hydrogen atoms in the molecule, the only important ones being the paraffins, the olefines, the acetylenes, and the di-olefines.

The Paraffins.—This, the largest of all the groups, includes those hydrocarbons in which the carbon atoms are united only by single linkages (hence called saturated hydrocarbons), and which consequently contain the largest possible amount of hydrogen, the general formula being C_nH_{2n+2}. Its members are formed when carbonaceous matter decays or is decomposed by heat in the absence of oxygen at relatively low temperatures and consequently are found in the emanations from marshes, the gases escaping from ponds, the "blowers" of the coal pits, and in coal-gas, coal-tar, shale oil, etc., as well as in the natural gas of the petroleum districts and in petroleum—particularly that of Pennsylvania; while the higher members ($C_{38}H_{78}$, for example) occur as the minerals ozokerite, hatchettite, ceresine, etc.

Although the first three members of the series each exist in one form only, there are two butanes, three pentanes, and five hexanes, all of which are known, while the number of isomerides of the higher homologues theoretically possible is enormous, and for such a substance as

$C_{13}H_{28}$ no less than 802 formulæ can be devised. Of the higher paraffins comparatively little is known, few having been obtained in a state of purity, and it is probable that in most cases even the m. p. and b. p. have not been ascertained with any degree of accuracy.

The following table gives the physical constants of the normal paraffins, and is taken (with some additions) from Richter's "Organische Chemie" (11th edition, 1909).

	Formula	M. p.	B. p. at 760 mm.	B. p. at 15 mm.
Methane	CH_4	$-184°$	$-164°$	....
Ethane	C_2H_6	$-172°$	$-84°$	....
Propane	C_3H_8	....	$-45°$	....
Butane	C_4H_{10}	....	$1°$	....
Pentane................	C_5H_{12}	....	$38°$	....
Hexane	C_6H_{14}	....	$71°$	....
Heptane ....:..	C_7H_{16}	....	$98.4°$	....
Octane	C_8H_{18}	....	$125.5°$	....
Nonane	C_9H_{20}	$-51°$	$149.5°$	....
Decane	$C_{10}H_{22}$	$-32°$	$173°$	....
Undecane	$C_{11}H_{24}$	$-26.5°$	$194.5°$	....
Dodecane	$C_{12}H_{26}$	$-12°$	$214°$	....
Tridecane	$C_{13}H_{28}$	$-6.2°$	$234°$	....
Tetradecane	$C_{14}H_{30}$	$+5.5°$	$252.5°$	....
Pentadecane	$C_{15}H_{32}$	$+10°$	$270.5°$	....
Hexadecane	$C_{16}H_{34}$	$+18°$	$287.5°$	....
Heptadecane	$C_{17}H_{36}$	$+22.5°$	$303°$	$170°$
Octadecane	$C_{18}H_{38}$	$+28°$	$317°$	$181°$
Nonadecane	$C_{19}H_{40}$	$+32°$	$330°$	$193°$
Eicosane	$C_{20}H_{42}$	$+36.7°$	....	$205°$
Heneicosane	$C_{21}H_{44}$	$+40.4°$	....	$215°$
Docosane	$C_{22}H_{46}$	$+44.4°$	....	$224°$
Tricosane	$C_{23}H_{48}$	$+47.7°$	....	$234°$
Tetracosane	$C_{24}H_{50}$	$+51.1°$	....	$243°$
Heptacosane	$C_{27}H_{56}$	$+59.5°$	....	$270°$
Hentriacontane	$C_{31}H_{64}$	$+68.1°$	....	$302°$
Dotriacontane	$C_{32}H_{66}$	$+70.0°$	....	$310°$
Pentatriacontane	$C_{35}H_{72}$	$+74.7°$	....	$331°$
Octatriacontane	$C_{38}H_{78}$	$+79.4°$	....	....
Hexacontane	$C_{60}H_{122}$	$+102°$	....	....

The paraffins are not attacked by chlorine in the dark, nor are they absorbed by bromine or by sulphuric acid, and so can easily be separated from the other aliphatic hydrocarbons; they are hardly attacked at all by fuming nitric acid or by chromic acid in the cold, although even dilute nitric acid converts normal hexane, heptane, and octane into nitro-paraffins on warming. (See Konowalow, Compt. rend.,

1892, **114**, 26; Ber., 1895, **28**, 1852; Worstall, Amer. Chem. J., 1898, **20**, 202; 1899, **21**, 210; Francis and Young, Trans., 1898, **73**, 928.) In daylight chlorine attacks them vigorously giving substitution products, bromine less readily, and iodine has no action.

Detection and Estimation of Paraffins.—Paraffins in the vaporous or gaseous state can be separated from hydrocarbons of the olefine and acetylene series by treatment in the dark with excess of bromine. The paraffins remain unaffected, while the unsaturated hydrocarbons are converted into liquid bromine compounds. The same principle is also applicable to liquid mixtures of paraffins and olefines. The unchanged paraffins may be separated from the olefine bromides by distillation in a vacuum.

When paraffins are heated with bromine and water for some time in sunlight, they are converted into bromo-substitution compounds, half the bromine which enters into action being afterwards found as hydrobromic acid. This behaviour may, under favorable circumstances, be employed for their recognition and quantitative estimation.

Liquid paraffins may also be separated from hydrocarbons of other series by treating the mixture first with sulphuric acid, so long as the acid becomes coloured, and then with fuming nitric acid, avoiding rise of temperature. Other substances are oxidised, or converted into nitro-compounds which remain dissolved by the acids or are much less volatile than the unaltered paraffins. After washing with water, drying over caustic potash, and rectification over sodium, a distillate of pure paraffins is obtained. A practical use of this principle is sometimes made in analysis.

THE OLEFINES, $C_n H_{2n}$.

The olefines closely resemble the paraffins in their physical properties, and are converted into them by nascent hydrogen; containing less hydrogen, they are "unsaturated compounds," and hence unite very readily with bromine (even in the dark), the halogen acids, concentrated sulphuric acid, etc.

Estimation of Olefines.—The only methods practically available for the direct and accurate estimation of olefines, when in admixture with hydrocarbons of other series, are based on the facility with which they unite with bromine, or their absorption by fuming sulphuric acid.

For the estimation of the *gaseous olefines*, as existing in coal-gas, a known measure of the gas is introduced into a graduated Cooper's tube, care being taken that the water which is displaced has been previously saturated with gas of the same quality. Bromine is then dropped into the water which remains in the curved part of the tube, the tube closed with a stopper or the thumb, and the contents well agitated. On opening the tube under water, the diminution of the volume of the gas will indicate that olefines have been absorbed, and, on observing the water, oily globules of $C_2H_4Br_2$ etc., will be perceived. These should be red or yellow in colour; if colourless, more bromine must be added and the agitation repeated. The tube being again opened under water, a small piece of sodium hydroxide is added to absorb free bromine and the tube agitated once more. The tube is then immersed in a cistern having glass sides, so that the volume of the residual gas can be read off when the water in the cistern is on the same level with that in the tube. The loss of volume, duly corrected, if necessary, for temperature and pressure, gives the hydrocarbons absorbable by bromine.

Satisfactory estimations of olefines can also be made by means of Hempel's gas-burette or Lunge's nitrometer. Hempel (*Methods of Gas Anal.*) states that the sulphuric acid method is the most accurate.

When the proportion of olefines is small, a known measure of the gas can be caused to bubble through a solution of bromine in carbon disulphide.

For the estimation of the olefines in *liquid hydrocarbons* the bromine method is still available, but the method of operating must be modified. The following modification of the process of Mills and Snodgrass (Vol. 2) has been extensively employed in Allen's laboratory and found very useful for the examination of commercial products from shale and petroleum. An approximately decinormal solution of bromine is made by dissolving 2 c.c. of bromine in 750 c.c. of recently distilled carbon disulphide. This solution, which keeps well in the dark, is rendered anhydrous by the addition of some lumps of dry calcium chloride An accurately weighed or measured quantity of the dry hydrocarbon, weighing between 0.3 and 1.0 grm., or a volume of a solution of the oil in carbon disulphide contaning a known weight of the hydrocarbon, is then placed in a perfectly dry stoppered flask or separator, the solution diluted, if necessary, with carbon disulphide (kept over calcium chloride) to about 25 c.c., and then 25 c.c. of the

carbon disulphide solution of bromine added. The flask is then closed, and the contents agitated. If the liquid is distinctly red, sufficient bromine has probably been added, but should the solution be nearly or quite decolourised, a further addition of a known measure of the bromine solution should be made without delay. The flask is then at once placed in the dark and kept there for a quarter of an hour, when an excess of an aqueous solution of potassium iodide is poured in, the contents agitated, the flask removed to a light place, and the solution titrated with a decinormal solution of sodium thiosulphate (24.8 grm. of crystallised salt per litre). The end of the action is indicated by the decolourisation of the carbon disulphide, and is rendered sharper by adding a few drops of starch solution toward the end of the titration.

25 c.c. of the carbon disulphide solution of bromine are then placed in a similar flask, potassium iodide solution added, and the titration with thiosulphate conducted as before. The difference between the volume of standard thiosulphate now required and that previously employed for the titration in presence of the hydrocarbon is the measure of thiosulphate corresponding with the bromine which has combined with the unsaturated hydrocarbons present. 1 c.c. of decinormal thiosulphate corresponds with 0.008 grm. of bromine. The bromine solution keeps for a considerable time without change, and hence the verification of its strength is only occasionally necessary.

It is absolutely necessary not to expose the hydrocarbon to the action of bromine in presence of strong light; even a very moderately diffused daylight is prejudicial, but gaslight has no sensible effect. Fifteen minutes should be allowed for the completion of the action. If much exceeded, secondary changes are liable to occur, which give results in excess of the truth, more or less hydrogen bromide being usually produced, the amount increasing with the time allowed for the action. On the other hand, the combination with bromine is sometimes not completed immediately. McArthur (*J. Soc. Chem. Ind.*, 1888, **7,** 65) points out that moisture must be rigorously excluded, the bromine added must be twice the quantity required for absorption (ascertained by a preliminary experiment), and the oil solution must be diluted with carbon disulphide to three times the volume of the bromine solution that is to be added.

The foregoing process gives tolerably concordant results, and was adopted by Allen in place of a method described by himself, in which the bromine was employed in aqueous solution. In

its simplest form this process is conducted exactly in the manner just described, except that approximately decinormal aqueous bromine is used, instead of a carbon disulphide solution of that element, and the potassium iodide solution is added directly after the oil has been thoroughly shaken with the bromine water. If the bromine compounds formed are viscous and adhere strongly to the sides of the flask, so as to hinder the action of the bromine water, a few centimetres of carbon disulphide may be added, by which the oils will be dissolved, and may be brought in contact with the bromine water by agitating. This method gives fairly constant results, but they do not represent simply the bromine assimilated by the unsaturated hydrocarbon, etc., of the sample, as oxidation also occurs to a very sensible extent. The results obtained are therefore in excess of those given by the carbon disulphide process, but they are fairly comparative, and for works-assays of shale and petroleum products the method will be found of service.

Owing to the complex character of commercial hydrocarbons, an estimation of the amount of bromine combining with them does not give the means of calculating the percentage of olefines present. If, however, a fraction of constant b. p. be prepared and its vapour density ascertained, its mean combining weight can be deduced, and an estimation of its power of assimilating bromine gives a means of obtaining a close approximation to the proportion of olefines contained in the fraction. This suggested method assumes that the fraction consists essentially of paraffins and olefines. Any admixture of hydrocarbons of other series would further complicate the problem.

On this account it is preferable in practice to express the results of titrations as bromine absorptions; that is, in grams of bromine assimilated by 100 grm. of the oil. If a known volume of the sample has been employed, the number of grams of bromine taken up by 100 c.c. must be divided by the density of the sample to ascertain the bromine assimilated by 100 grm.

It must be borne in mind that, besides olefines, many other substances, both hydrocarbons and oxygenated substances, assimilate bromine, and hence the "bromine absorption" of a complex mixture arises from several sources. Nor does the bromine absorbed by substances other than olefines bear a constant relation to their molecular weight. Thus the hydrocarbons of the acetylene series absorb either

Br_2 or Br_4, and the latter proportion is also assimilated by terpenes. Oleic acid combines with Br_2, linoleic acid with Br_4, and phenol with Br_6, a bromo substitution product being formed in the last case. The results given by these substances are described in the sections on oleic acid, turpentine oil, phenol, etc.; and estimation of the bromine absorptions of shale and petroleum products, rosin oil, and resins will also be found duly recorded.

It is possible to ascertain the iodine absorption of hydrocarbons by Hübl's method, which gives results comparable with those obtained by bromine if the former be multiplied by the factor 0.63. The process is, however, not well adapted for the examination of hydrocarbons, as the action may not be complete in less than twenty-four hours.

THE ACETYLENES, C_nH_{2n-2}.

The members of this group are usually oily liquids of rather higher b. p. than the corresponding paraffins; they are, of course, un-saturated compounds, containing a triple linkage, and react with hydrogen, the acids, halogens, etc., in very much the same manner as the olefines. Their most characteristic property is the great readiness with which they react with ammoniacal solutions of cuprous or silver salts, forming compounds such as $C_2H_2.Cu_2O$ which are almost always thrown down as precipitates. By this property they can be distinguished and separated from all other hydrocarbons.

The cuprous solution is prepared by treating copper turnings in a separator with strong ammonia in presence of a limited quantity of air, until the blue liquid first formed has become colourless. The reagent is then run from the tap into a U-tube fitted with a tube bent twice at right angles, the open end of which dips under water, so as to prevent contact of air. On passing a gas through the cuprous solution, a yellow or red precipitate will be produced if acetylenes be present. If the precipitate be filtered from the liquid and treated with strong hydrochloric acid, the acetylene will be liberated. This behaviour furnishes a means of isolating acetylene and its homologues in a condition of purity. On treating the cuprous compound with aqueous ammonia and zinc, the corresponding olefine will be produced, and may be identified by the proportion of bromine with which it unites.

The silver derivatives of the acetylenes may be obtained by substituting an ammoniacal solution of silver nitrate for the cuprous solu-

tion. A solution prepared by dissolving cuprous or silver chloride in ammonium hydroxide *absorbs* acetylenes, but some of the hydrocarbons are not *precipitated* by such a reagent, as their metallic derivatives are soluble in ammonium hydroxide containing ammonium chloride.

Acetylene, C_2H_2, is an important illuminating agent. It may be prepared in various ways, but the only one of moment is the action of water on calcium carbide, by which calcium hydroxide and acetylene are the only products. Acetylene is a colourless gas with a faint ethereal odour; it is usually regarded as highly poisonous, but several investigators deny this. As prepared from commercial calcium carbide it is very impure, and the disagreeable odour and poisonous action attributed to the acetylene itself are due to the impurities, especially hydrogen phosphides and sulphur compounds. The statement that acetylene causes the odour and annoyance developed by the imperfect combustion of illuminating gas, as when a Bunsen burner "strikes back," is, therefore, not correct. The following data concerning the manufacture and properties of commercial acetylene are mostly taken from a paper by H. Fowler (*Proc. of the (British) Institute of Civil Engineers*, No. 3093, Mar., 1898):

1 pound of pure calcium carbide will require 0.562 pound of water and yield 1.156 of slaked lime and 0.4064 of acetylene, equal to 5.5857 cu. ft. at 0° and 760 mm. The yield of good commercial carbide is about 5 cubic feet per pound. Water dissolves about 1.1 times its volume, but a saturated solution of common salt dissolves only about 0.05 volumes. Alcohol dissolves about 6 volumes and paraffin about 2.5; acetone dissolves a large amount. Since the density of acetylene is nearly that of air, it diffuses slowly, hence the danger of formation of explosive mixtures in the neighbourhood of a leak. The most violent explosion is produced by a mixture containing 8.37 per cent. by volume of the gas. Acetylene is liquefied at 0° by a pressure of 21.5 atmospheres; at 20° by a pressure of 42.8 atm. The critical temperature is 37.05° at 68 atm.

Liquid acetylene has a sp. gr. of 0.4 and is highly expansible. It is liable to explosive dissociation, and the conditions under which this occurs have been extensively studied. Berthelot and Vieille placed 18 grm. of acetylene in a small flask and fired the mass by means of a wire rendered incandescent by an electric current. The pressure rose to 5638 atmospheres, and the carbon was left as a lump with brilliant surface and conchoidal fracture. Explosion may also be brought

about by fulminating powder and even by friction. The presence of spontaneously inflammable hydrogen phosphide (PH_2) is said to have been the cause of at least one explosion. To remove this objectionable ingredient, Pictet uses a washing solution of strong calcium chloride, and then a lead salt at —16°, but even this treatment may not remove all the phosphide. The following are analyses of ordinary acetylene:

	Fowler	Outon
Acetylene.................................	95.6	98.74
Hydrogen sulphide	trace	1.03
Hydrogen phosphides	0.038	0.23
Ammonia	0.03	....

Acetylene can be estimated by titrating the free nitric acid produced by the action of the gas on a solution of silver nitrate.[1] The change is represented as follows:

$$C_2H_2 + 3AgNO_3 = C_2Ag_2.AgNO_3 + 2HNO_3.$$

The mixture must not contain any gases which interact with nitric acid or which are themselves acid in character, and the silver nitrate must be in excess. The only data necessary for the calculation are the volume, temperature, and pressure of the gas, and the final volume and acidity of the liquid. The operation may be performed in a Raoult eudiometer, 20 c.c. of a 10% solution of silver nitrate sufficing for a 60 c.c. eudiometer, distilled water being afterward run in until the pressure is equalised.

The most serious impurity of acetylene, as prepared by the action of water on commercial calcium carbide, is hydrogen phosphide, which, like ammonia, appears to favour the formation of the explosive copper acetylide, and, if present in notable quantity, may render the gas spontaneously inflammable. The hydrogen phosphide may be estimated by passing the gas, as it is liberated, through a solution of sodium hypochlorite, and precipitating the phosphoric acid formed by means of magnesia mixture. If care be taken that all the reagents are free from sulphates, the hydrogen sulphide in the acetylene may be estimated by acidifying the filtrate from the magnesium precipitate and adding barium chloride. It should be observed that the amount

[1] Chevastelon. Compt. rend., 1897, 125, 245.

of hydrogen sulphide in different specimens of acetylene yielded by the same calcium carbide varies considerably, according to the conditions obtaining at the time of preparation. Moreover, the whole of the sulphur in the gas does not exist as hydrogen sulphide.

P. W. Wolff (*Chem. Zeit.*, 1898, **22,** 281) states that the tendency of acetylene to produce soot can only be avoided by the use of special burners, and that the employment of hypochlorites for removal of hydrogen phosphides, as recommended by Lunge and Cedercreutz, will involve danger when notable amounts of ammonia are present in consequence of the formation of nitrogen chloride. The ammonia should be first removed by thorough washing. Chlorine and moisture may be removed by subsequent treatment with lime. Acetylene thus purified has a faint ethereal odour, and does not attack copper or copper alloys. The stains on copper fittings when common acetylene is used are due to copper phosphide.

Lewes (*J. Gas Lighting*, Nov. 30, 1897) states that acetylene is much safer when diluted with other combustible gases. The best diluent is a mixture of 30% methane with hydrogen, carbon monoxide, or both. This diluting gas when mixed with 10% of acetylene is a convenient substitute for coal-gas.

Hempel and Kahl (*Zeit. für ang. Chem.*, 1898, **11,** 53) suggest a volumetric method for estimating hydrogen phosphide in acetylene. A solution of 15.6 grm. of copper sulphate ($CuSO_4$, $5H_2O$) in 100 c.c. of water, to which were added 5 c.c. of dilute sulphuric acid (1 volume of concentrated acid to 4 volumes of water), was found to be the best absorbent. One c.c. of the solution absorbed 8.8. c.c. of hydrogen phosphide and 0.2 c.c. of acetylene from 100 c.c. of each gas. In the presence of mercury and excess of the solution of copper sulphate, the diminution of volume resulting from the absorption of hydrogen phosphide exactly corresponded to four times the volume present. Hydrogen phosphide produced by heating an alcoholic solution of potassium hydroxide with ordinary phosphorus was mixed in various known proportions with nitrogen, and the phosphide determined. The mean value was 52.4 per cent., and mixtures of known volumes of this mixture and acetylene were examined by agitating it for three minutes, in a pipette sealed with mercury, with 3 c.c. of the copper sulphate solution. It was assumed that the hydrogen phosphide amounted to 1/4 of the diminution of volume. The test analyses were satisfactory.

Detection of Acetylene in Cases of Poisoning.—D. Vitali

(L'Orosi, 1898, **21**, 217) recommends the following method: A sample of blood is mixed with 5 or 8% of pure dry acetone, placed in a retort, and distilled into an empty condenser and a set of absorbing bulbs containing more acetone. The retort is heated on a water-bath, the condenser and bulbs kept cold in ice. The acetone passes over, carrying the acetylene with it, and the latter may be identified by its characteristic reactions. Hydrogen sulphide and phosphide, which often occur in the crude gas, also dissolve in the acetone, and can be sought for therein.

Calcium carbide is prepared by the action of an electric current upon a mixture of quicklime and carbon (coke or anthracite coal). Pure calcium carbide is brown, but the commercial form is a hard, grayish, slag-like mass, which, when exposed to the air, usually emits an odour of hydrogen phosphide, and slowly crumbles to a dry powder. It is often irregular in quality. A considerable proportion of free carbon may often be observed in it, and great care must be taken in sampling. Water acts violently on calcium carbide, but a strong aqueous solution of zinc chloride acts much more slowly. Calcium carbide may be used for the detection and estimation of water in alcohol, since absolute alcohol is without action upon it.

A method for the assay of calcium carbide has been published by Lunge and Cedercreutz (*Zeit. ang. Chem.*, 1897, **10**, 651). 100 grm. of the material should be used. The apparatus is a gas holder having a capacity of 40 litres, a saturated solution of common salt being employed as a seal. In exact work this must be previously saturated with acetylene. If plain water be used as a seal, a correction must be made for the acetylene absorbed. The action is most conveniently carried out in an apparatus arranged to cause the carbide to fall into the salt solution by degrees, but the reverse process may be employed.

Two samples of calcium carbide examined by Lunge and Cedercreutz evolved, as the mean of several tests, 0.1435 grm. (94.1 c.c.) and 0.338 grm. (222 c.c.) of hydrogen phosphide per kgm. of carbide, respectively.

Destructive Distillation.—Non-volatile organic substances heated without access of free oxygen undergo complex decomposition, by which volatile products escape and a residue of impure carbon, is left. If the substance consists only of carbon, hydrogen, and oxygen, the last two elements are found in the distilled portions, together with a great part of the carbon. Sulphur and nitrogen are

also principally converted into volatile compounds. Slow heating will sometimes produce volatilisation with little or no change. The nature and proportions of the substances obtained will be dependent on the character of the substance distilled, the temperature of the retort, and other conditions; when the heat is moderate, paraffins are chiefly produced; but as the higher members of this series readily split up into lower members and olefines, the latter are nearly always present. By further degradation acetylenes are formed, while benzene and its homologues contain a still smaller proportion of hydrogen.

When the temperature is high, hydrogen, acetylene, benzene, and naphthalene are the chief unoxygenated products. Thus, *coal* being distilled at a high temperature for the manufacture of coal-gas, the condensable hydrocarbons consist chiefly of benzene and its homologues, naphthalene, etc. At a somewhat lower temperature the hydrogen and acetylene disappear, together with most of the naphthalene, while chrysene and a larger proportion of benzene are formed.

At a dull red heat, such as is employed for the distillation of bituminous shale, the liquid products are almost free from benzene and naphthalene, while little or no hydrogen or acetylene is present in the gases. On the other hand, the distillate is rich in paraffins and olefines with some anthracene and chrysene; the oxygenised and nitrogenised products consist chiefly of substances of the formula $C_nH_{2n-7}OH$, and other phenolic compounds, and bases of the formula $C_nH_{2n-5}N$ (pyridine bases), although the corresponding series, C_nH_{2n-6}—*i. e.*, benzene and its homologues—is almost wholly absent.

When *wood* is subjected to dry distillation, the volatile products are practically free from compounds of nitrogen and sulphur. The watery portion of the distillate from wood, peat, and lignite has an *acid* reaction, owing to the presence of acetic acid. In other respects the products of the distillation of wood, as ordinarily conducted, are a mixture of low- and high-temperature products.

When the temperature of the distillation is low, a large yield of liquid products is usually obtained, together with a small yield of gas of high illuminating power. At a high temperature a maximum production of gas of low illuminating power results, while the proportion of liquid products is small. The higher the temperature of the retort, the larger the percentage of solid carbonaceous residue (coke or charcoal) left in it.

The three cases afforded in practice by the treatment of coal, shale, and wood may be regarded as typical of the changes attending the destructive distillation of organic substances, though others, such as bone, rosin, and oil, yield special products of some practical interest. Too much stress cannot be laid on the fact that the nature of the products depends not only on the nature of the substance treated, but also on the circumstances under which the operation is conducted with regard to temperature and other conditions.

The following table indicates the general nature of the more prominent volatile organic products of the dry distillation of coal (for the manufacture of illuminating gas), bituminous shale, and wood, *as the processes are carried on in practice.* To facilitate comparison, the leading constituents of American petroleum are shown in juxtaposition:

Organic products	Coal	Bituminous shale	Wood	Petroleum
Hydrogen,	Large,	Traces,	Large,	Present.
Gaseous Hydrocarbons.				
Methanes	Large,	Large,	Large,	Present.
Olefines	Large,	Large,	Considerable	Present.
Acetylenes	Present,	None.	....	....
Liquid and Solid Hydrocarbons.				
Liquid paraffins	Small,	Large,	Absent,	Very large.
Solid paraffins	Traces,	Considerable	Present,	Moderate.
Liquid olefines	Small,	Very large,	....	Considerable
Liquid pseudolefines	....	....	....	Present.
Liquid acetylenes	Present,	Present.	....	....
Benzenes	Large,	Trace,	Moderate,	Present.
Naphthalene	Large,	None,	Moderate,	None.
Anthracene	Moderate,	Trace,	....	Present.
Chrysene	Moderate,	Considerable	Present,	Present.
Oxygenated Bodies.				
Acetic acid	Present,	Present,	Large,	....
Methyl alcohol	None,	....	Considerable	....
Phenols	Large,	Considerable	Moderate.	....
Hydroxyphenols (creosote)	....	Large,	Large,	....
Nitrogenised Bodies.				
Ammonia	Considerable	Considerable	None.	....
Aniline bases	Present,	None.	....	....
Pyridine bases	Considerable	Considerable	....	....
Acridine	Present.	....	....	....
Carbazole	Present.	....	....	....
Sulphur Compounds,	Present,	Present,	None,	Present.

It will be seen from this table that the products of the distillation of each of the raw materials contain certain characteristic bodies. Thus, oxygenated products are found most largely in the products of the distillation of wood; paraffins are *especially* characteristic of petroleum; olefines, and, to a lesser extent, paraffins, of the distillation of shale;

while coal-tar, as obtained in the manufacturing of illuminating gas, is remarkable for the comparatively large proportion of benzene and naphthalene contained in it.

TARS.

By the destructive distillation of organic substances and bituminous minerals three classes of products are generally obtained—namely, gas, watery liquid, and a viscid, dark-coloured oil or tar. The methods of assaying the gaseous products do not come within the scope of this work. The watery liquid from wood, peat, and lignite is acid, and its examination is described in Vol. 1. The watery liquid from the distillation of coal, shale, and bones is strongly alkaline, the first of these constituting the "ammoniacal liquor" of the gas works.

TAR is a brown or black viscid, oily liquid, of a more or less characteristic odour, according to its origin; its composition varies widely according to its source and the conditions of distillation. Wood, peat, and lignite tars are acid; coal, bituminous shale, and bone tars are alkaline. On repeatedly agitating the tar with water, the soluble matters to which the acid or alkaline indication was due may be more or less completely removed.

All tars consist largely of hydrocarbons, but oxygenised and nitrogenised substances are sometimes present in considerable proportion. All tar, being of very complex composition, and consisting in the main of volatile bodies, the most instructive method of examining it consists in subjecting it to careful distillation, collecting apart the distillates obtained at different temperatures, and subsequently fractionating these products with the view of effecting a more perfect proximate analysis of the material. Toward the end of the distillation the tar remaining in the retort becomes more and more viscous, and if allowed to cool, sets to a solid, brittle, jet-black mass known as *pitch*. If the distillation be pushed further, *coke* is obtained, and, indeed, in some cases distillation always causes coking.

Tar frequently contains a considerable proportion of water which should be separated as far as possible before distillation. This is best effected by allowing the tar to stand in a warm place, giving the mass an occasional gyratory motion, and removing each quantity of water by decantation as it separates. Water causes tar to froth during distillation; Mallmann ("Bitumen," 1909, **7,** 117) states that a tar from

which water readily separates on standing will be difficult to distil, and
vice versa.

For the method of conducting the distillation, no general instruc-
tions can be given; much depends on the character of the tar, the
information desired, the scale on which the operation is to be con-
ducted, and other conditions. The process should be conducted in
the simplest suitable apparatus, and the distillate collected in a very
moderate number of fractions, all refinements of fractional distilla-
tion being reserved for the treatment of the products first obtained.
In the first distillations the more volatile constituents are retained in
the retort by those of higher b. p., and it is only after being separated
tolerably perfectly from these that they distil at temperatures approxi-
mating to their true b. p.

The separation by fractional distillation having been carried out
as far as appears desirable, a further proximate analysis of the dif-
ferent fractions may be made into basic, acid, and indifferent bodies.
Thus, by agitating one of the fractions with dilute sulphuric acid, any
basic compounds (*e. g.*, ammonia, methylamine, pyridine, acridine, etc.)
will be dissolved in the acid liquid, and can be recovered by appropriate
means. On agitating the residual oil with sodium hydroxide solution,
first dilute, and then somewhat concentrated, any organic acids, phenols,
or phenolic compounds will be dissolved, and can be recovered by sepa-
rating the alkaline liquid and adding a slight excess of dilute sulphuric
acid. The neutral substances which have not undergone solution either
by the treatment with acid or with alkali consist essentially of hydro-
carbons. Particular processes are suitable for special purposes.
Thus, benzene may be crystallised out by subjecting the more volatile
fraction of coal-tar naphtha to a freezing mixture; naphthalene readily
separates from oils containing it, especially after removal of the
phenols by sodium hydroxide; while the presence of anthracene can
be inferred from the formation of anthraquinone by the oxidation
of a certain high-boiling fraction of the tar. The hydrocarbons of
the different series may be successfully differentiated in many cases by
their behaviour with reagents, especially with bromine, nitric acid, and
strong sulphuric acid.

The following sections contain detailed descriptions of the char-
acters and methods of examining tar from bituminous shale and coal.
Tars of some other origins are also briefly described.

SHALE TAR. CRUDE SHALE OIL.

The crude oily liquid obtained in the south of Scotland by the destructive distillation of bituminous shale is an olive-green, strongly-smelling, viscous liquid. The sp. gr. of the product from the old form of retorts is 0.890 to 0.894, and from the new kind 0.865 to 0.870. The composition of shale oil has not been so thoroughly investigated as that of coal-tar, but it has been proved to be of extremely complex nature, the following being among the more characteristic and important substances hitherto recognised in it:

Hydrocarbons of the Methane series; most of the members from C_4H_{10} to $C_{30}H_{62}$ being probably present.

Hydrocarbons of the Olefine series; most of the members from C_4H_8 to $C_{20}H_{40}$ being probably present.

Hydrocarbons of the Allylene series; e. g., C_6H_{10}, C_7H_{12}, and C_8H_{14}.

Hydrocarbons of the Benzene series; present only in small amount, but always found in the oils from modern retorts.

Only traces of naphthalene and anthracene are found in shale tar, but notable quantities of pyrene and chrysene occur.

Nitrogenised compounds. Shale tar contains ammonia, a considerable proportion of pyrroline, and members of the pyridine series (especially those of high b. p. and unknown constitution), but neither aniline nor any of its homologues has been detected.

Oxygenated compounds. Besides traces of acids of the acetic series, shale tar contains a notable proportion of phenols and hydroxyphenols analogous to those present in wood-tar. Thymols and analogous bodies have been found in the fraction distilling between 215° and 290°.

Sulphur compounds exist in shale tar, but their exact nature has not been ascertained. Shales containing much sulphur give little paraffin wax on distillation, and a low yield of other products.

The method of treating shale tar on a large scale differs in different works, but consists essentially in repeated fractional distillations, alternated by treatment of the several fractions with sulphuric acid and sodium hydroxide, and sometimes sodium carbonate, together with refrigeration of the high-boiling fractions to cause the crystallisation of solid paraffin. This is separated from the adhering oil by pressure, and the crude paraffin scale which results is purified by appropriate methods.

Assay of Crude Shale Oil.—The examination of crude shale oil is

frequently required, in order to ascertain the proportions of naphtha, burning oil, lubricating oil, and "scale" or crude paraffin wax it is likely to yield on a large scale. The assay is best made by treating a known quantity of the oil as nearly as possible in the same manner as that employed in the manufacturing process, but working on the small scale losses are, of course, very much larger; to diminish these as far as possible all vessels, cloths, etc., are rinsed with oils similar to those to be handled, and the quantities of acid and alkali used are smaller than in the works. Each oil works has its own method of analysis, but the general features of the methods are similar, and all use measurements in preference to weights, and divide their fractions in a somewhat arbitrary manner. In a works laboratory the analyst knows fairly well what to expect from a particular sample, but when dealing with a strange oil it is best to make a preliminary test by distilling a portion without steam, collecting all below 150° as "spirit"; from 150° to 300° as "burning oil," and all above 300° (the thermometer having been withdrawn) as heavy oils. The following notes are due to the kindness of one of the best known of the Scottish oil chemists. In this process all measurements are calculated to 60° F.; the oils are usually measured at higher temperatures, and the necessary correction made (the sp. gr. is lowered 0.004 by each rise of 10° F. above 60° F.); the solid paraffin is weighed and its volume calculated, the sp. gr. in the liquid state at 60° F. being taken as 0.810.

1,300 c.c. (20,000 fluid grains) of crude oil freed from water by standing at 120° F. are distilled from a copper or cast-iron still, in a slow current of superheated steam; this distillation being destructive, excess of steam causes too much oil to pass over unchanged, and the subsequent treatments give misleading figures. 1,000 fluid grains of distillate are taken as "green naphtha," the remainder as "green oil," though some crude oils give, toward the end, so much "gundy" (chrysene, etc.) that this is kept separate; "still coke" remains in the retort. The green oil—in a stoppered bottle—is well shaken for 5 minutes with 0.25% of oil of vitriol (to remove moisture); then, at a temperature of 100 to 105° F., it receives 2% oil of vitriol, is shaken for a further 5 minutes and allowed to settle for 2 or 3 hours at 100 to 120° F. Next, the oil is washed with an excess of sodium hydroxide solution of 60° Tw. (1.300 sp. gr.), allowed to settle in a warm place, the alkali tar removed, and the oil again distilled with superheated steam—40% being collected as "light oil" and the remainder as "heavy oil and

paraffin." The heavy oil is cooled slowly (to obtain large crystals), first to the room temperature, then in a freezing mixture, wrapped in a cloth previously wrung out with "blue oil" and pressed at 60° F., giving solid paraffin ("hard scale") and "blue oil." The blue oil, after treatment with 0.5% of oil of vitriol and with sodium hydroxide, is distilled with 1% of dry sodium hydroxide, yielding light oil and lubricating oil; the 2 light oils—from the "green oil" and the "blue oil"—are mixed, treated with 0.25% oil of vitriol and sodium hydroxide, and again distilled. yielding burning oil and intermediate oil; the intermediate oil, treated like the heavy oil, gives a further yield of solid paraffin ("soft scale").

The methods of examining the naphtha, burning oil, lubricating oil, and paraffin scale which form the proximate products of the distillation of crude shale oil are described in the section on "Petroleum and Shale Oil Products."

Blast-Furnace Tar.

The tar produced by cooling waste-gases from blast furnaces consuming bituminous coal has been examined by Watson Smith (*J. Soc. Chem. Ind.*, 1883, **2**, 495 and 1887, **6**, 583). The sample had a sp. gr. of 0.954, and on distillation gave the following results:

	Percentage of products	Sp. gr.
Distillate below 230°	{ Water, 30.6 by volume.	1.007
	{ Oil, 2.9 by volume.	.889
Distillate from 230° to 300°..........	7.0 by volume.	.971
Distillate from 300° till oils solidify....	13.0 by volume.	.994
Distillate solidifying on cooling, or soft paraffin scale.	16.7 by volume.	.987
Coke	21.5 by weight.	....
Loss	5.5 by weight.	....

On further fractionation and treatment with sulphuric acid and sodium hydroxide the following products were obtained:

	Per cent. by volume
Tar bases, soluble in sulphuric acid	10.6
Phenols and tar-acids, soluble in sodium hydroxide............	5.6
Neutral oils	18.2
Soft paraffin scale	5.7

(Yielding solid paraffin, 0.54%.)

The phenolic compounds are further described under the head of "Blast Furnace Creosote."

Of the neutral oils, only an insignificant fraction distilled below 180°. The sp. gr. of successive fractions rose from 0.858 to 0.980. No naphthalene could be separated from an appropriate fraction by cooling it with ice and salt. The intermediate oils are not specially good as lubricants, nor are they suitable for burning in lamps. The fractions distilling between 250° and 350° possessed a deep green fluorescence, and closely resembled heavy lubricating oil from shale. On treating the soft paraffin scale with glacial acetic and chromic acids, solid paraffin was obtained, and a large proportion of a pitchy deposit was formed, but no anthraquinone, produced by the oxidation of anthracene, could be detected.

Wood-Tar.—The products of the destructive distillation of wood are very numerous, and vary much with the nature of the wood and the temperature at which the process is conducted. But under all circumstances the volatile products are characterized by the large proportion of oxygenised products contained in them, and by the small proportion of sulphur and nitrogen compounds. Among the gaseous products are carbon dioxide, carbon monoxide, hydrogen, and some methane. The aqueous portion of the liquid distillate, known as *crude pyroligneous acid*, usually forms from 28 to 50% of the weight of wood distilled, and contains chiefly acetic acid, methyl alcohol, allyl alcohol, and acetone, with many other substances in smaller proportion.

The "tar," or oily portion of the crude distillate from wood, averages from 7 to 10%, and is a complex mixture of various liquids holding solid matters in solution. On distillation between 70° and 250°, Russian wood-tar yields oils of a density ranging from 0.841 to 0.877, and leaves a residue of *pitch*, consisting of solid paraffin, various resinous matters, pyrene, chrysene, and other hydrocarbons of high b. p.

On redistillation the tar-oils yield the following products:

Below 100°; fatty acids, sylvane (C_5H_6O), methyl alcohol, benzene.
Between 100° and 150°; benzene homologues.
Between 150° and 200°; benzene homologues, phenols, and hydroxyphenols.
Between 200° and 250°; phenols and hydroxyphenols, lignoceric acid ($C_{24}H_{48}O_2$), naphthalene, retene, paraffin wax.

The lower paraffins appear to be absent from the tar, but the permanent gases produced by the distillation of the wood contain methane. If the oils of wood tar are exposed to a high temperature, they are

partially converted into heavy gaseous hydrocarbons. "Wood-gas is manufactured in this manner, and contains, when purified:

Hydrogen .... 48.7 to 18.7
Methane .... 35.3 to 9.4
Ethylene and its homologues.......................... 10.6 to 6.5
Carbon monoxide .... 61.8 to 22.3

80% of the more volatile portion of Swedish wood-tar consists of a mixture of 2 terpenes: australene, boiling at 155°; and sylvestrene, boiling at about 175°. The most important product from wood-tar is the mixture of phenolic compounds known as creosote, the method of examining and the nature of which are described later.

STOCKHOLM TAR, used in ship-building, is the product of a crude distillation of the resinous wood of the pine. It contains much resin and turpentine, and has applications for which the tar obtained in the manufacture of pyroligneous acid cannot be substituted. It has a sp. gr. of 1.04, and on standing usually deposits a granular, crystalline matter consisting mainly of *pyrocatechol*. Water agitated with the tar acquires a light brown colour and sharp, bitterish taste. The aqueous liquid is coloured transiently green by ferric chloride, owing to the pyrocatechol; lime water acquires a permanent brownish-red colour. When Stockholm tar is heated, water, acetic acid, and impure turpentine oil are volatilised and ordinary *pitch* remains.

COAL-TAR.

Coal-tar, being a product of destructive distillation, its composition varies with the details of the distillation, and there are marked differences between tars obtained in the manufacture of coal-gas, and those collected at the coke ovens; when coal-tar is mentioned without any qualification, that from the gas works is usually referred to.

Gas-works Tar.—This is a black viscid fluid, with a strong and chararacteristic odour; its sp. gr. ranges from 1.10 to 1.25, being most frequently between 1.15 and 1.21; at the present time (1909) owing to the higher temperatures employed in the carbonisation of coal, the average sp. gr. has an upward tendency.

The first treatment of coal-tar on a large scale consists in distilling it and collecting the distillate in three or four fractions. The temperatures at which the receivers are changed differ considerably in the practice of different works, and hence the products are far from being

identical. The following table represents three methods of fractiona-
tion which are largely employed:

A		B		C	
Product	Distilling point,°	Product	Distilling point,°	Product	Distilling point,°
Crude naphtha or light oils.	o to 170	First runnings, or first light oils	o to 110	Light naphtha.	o to 110
Heavy oils, dead oils, or creosote oils	170 to 270	Second light oils.	110 to 210	Light oil.......	110 to 170
		Carbolic oils...	210 to 240	Carbolic oils ...	170 to 225
		Creosote oils...	240 to 270	Creosote oils...	225 to 270
Anthracene oils,	above 270	Anthracene oils,	above 270	Anthracene oils.	270 to 360
Pitch...........	....	Pitch...........	....	Pitch..........	....

The arrangement on page 23, taken with certain alterations from
a table published by E. J. Mills, shows the general method of treating
coal-tar in works employing method C of original fractionation.

During the first part of the process permanent gases are given off,
while the fluid distillate consists of ammoniacal water and the most
volatile constituents of the tar proper, together with sensible traces of
less volatile bodies, carried over mechanically or volatilised in com-
pany with the steam, etc. The ammoniacal liquor forms a lower
layer which can be readily separated from the first light oils. The
point when the shoot should be changed is indicated pretty accurately
by a "break" or comparative cessation of distillation, together with a
peculiar noise known as "the rattles." On further heating the dis-
tillation recommences, and the second light oils come over regularly.
The point for again changing the shoot is, in some works, that at which
a sample of the distillate sinks in water, while in other cases the solidifi-
cation of the distillate on cooling, from the crystallisation of naphtha-
lene, is the indication relied on. At a higher temperature a distillate
is again obtained, which remains liquid on cooling. The commence-
ment of the anthracene oil period may be ascertained by a thermometer
immersed in the *vapour*, but is commonly deduced from the quantity of
the distillate. It may also be considered to commence at the point
at which the distillate again deposits solid matter on being completely
cooled. Sometimes the anthracene oils are subdivided into first and
second "green oils" and "red oil." The distillation is sometimes
stopped when the oil sets to the consistence of butter on cooling, but
may be pushed as far as possible short of actual coking, the residue
remaining in the retort consisting of hard pitch, which, after cooling, is

run out into tanks. Owing to the fall in the value of anthracene, however, the anthracene oil fraction is now rarely worked. The distillation is stopped at the end of the creosote oil period, and the anthracene left in the pitch, which then requires no addition of softening oil.

The proportions of the various products obtained necessarily vary largely with the character of the tar distilled and the details of the mode in which the operation is conducted. These differ in different works and in the same works at different times.

If the coal be distilled at a low temperature, a considerable amount of paraffins and other open-chain compounds are formed; distillation at high temperature increases the proportion of closed-chain hydrocarbons. At high temperature, however, much carbon is deposited in the free state by contact of the distilling substances with the hot walls of the retort. The resulting gas is, therefore, lighter than that produced at a low temperature. This fact is practically applied in filling large balloons. When possible, the engineer works a bench of retorts at a high temperature, and thus obtains a gaseous mixture containing more methane and free hydrogen, and hence of greater lifting power, than a gas from a lower heat. For yields of English tars, see pages 26 and 27.

The general composition of the various fractions obtained by the distillation of coal-tar will be regulated chiefly by the b. p. of the leading constituents, but the vapour-densities, vapour-tensions, and relative abundance of the constituents of the tar also largely affect their behaviour in the still. Thus, naphthalene is always found in notable quantity in all the fractions from second light oils to anthracene oil, and is even deposited from the purified illuminating gas itself. Owing to the high temperatures generally employed in the gas works at the present time, the quantity of naphthalene in all the fractions coming from the tar is very greatly increased, so that with most tars the light oil as well as the creosote fraction will completely solidify on cooling to the ordinary temperature.

Constituents of Coal-tar.—(For a full discussion of the constituents and products of coal-tar see M. Meyer, *Zeit. Angew. Chem.*, 1909, **22,** 338 and 391.) The following summary of the more important constituents of gas-works tar is compiled from Lunge's "*Coal-tar and Ammonia,*" third edition.

Coal-tar. Distil.

Ammoniacal liquor.

First light oils.

Naphtha.

Wash with 12% sulphuric acid (sp. gr. 1.85);

Wash with water.

Wash with 6% of sodium hydroxide solution (sp. gr. 1.10).

Distil purified oil.

Benzols. Distil.

Solvent naphtha to 0.875 sp. gr.

Illuminating oil to 0.900 sp. gr.

Bottoms (grease).

90% Benzol to 100°. 50% Benzol to 140°. Solvent naphtha to 170°.

Second light oils. Distil.

Intermediate; Distil.

Illuminating oil.

Solvent naphtha.

Solvent naphtha.

Carbolic oils to 225°.

Carbolic oil.

Wash with sodium hydroxide solution.

Phenates. Decompose with dilute sulphuric acid.

Carbolic acid.

Neutral oils. Distil.

Naphthalene.

Creosote oils to 270°.

Lubricating oil.

Anthracene oils. Cool, filter, and press.

Oil; Distil.

Anthracene cake.

Anthracene.

Pitch.

Pitch.

I. *Hydrocarbons.*

    a.   Paraffins, CH_4 to $C_{27}H_{56}$.
    b.   Olefines, C_2H_4 to C_7H_{14}.
    c.   Naphthenes, C_6H_{12} to C_8H_{16}.
    d.   Acetylenes, C_2H_2, etc.
    e.   Naphthylenes, C_6H_{10} to C_8H_{14}.
    f.   Terpenes, C_6H_8 to $C_{10}H_{16}$.
    g.   Benzenes, C_6H_6 to $C_{10}H_{14}$.
    h.   Naphthalenes, $C_{10}H_8$ to $C_{12}H_{12}$.
    i.   Anthracene and phenanthrene, and their homologues.
    k.   Pyrene, chrysene, picene, etc.

II. *Oxygen Compounds.*

    a.   Water.
    b.   Alcohols (?).
    c.   Acetone.
    d.   Acetic and benzoic acids.
    e.   Phenol and cresols.
    f.   Naphthols.

III. *Sulphur Compounds.*

    a.   Hydrogen sulphide.
    b.   Ammonium sulphide and thiocyanate.
    c.   Sulphur dioxide.
    d.   Carbon disulphide.
    e.   Thiophenes and thiotolenes, etc.
    f.   Mercaptans.

IV. *Nitrogen Compounds.*

    a.   Ammonia and its salts.
    b.   Alkylamines.
    c.   Anilines.
    d.   Pyridines, C_5H_5N to $C_{12}H_{19}N$ (?).
    e.   Quinolines, C_9H_7N to $C_{11}H_{11}N$.
    f.   Acridines.
    g.   Pyrrole.
    h.   Cyanides and methyl isocyanide.
    i.   Carbazoles, $C_{12}H_9N$, etc.

Assay of Coal-tar.—The assay of coal-tar is usually limited to a laboratory operation in which the various fractions are collected as nearly as possible under the same conditions as those which obtain on the large scale, though the details will necessarily vary with circumstances. With practice, good results are obtained with as small a quantity as 10 ounces of the tar, the yields corresponding closely with those given on a large scale; but the chief value of such laboratory operations is for *comparing* different samples of tar. The following mode of operation is that recommended by B. Nickels: 250 c.c. or 10 ounces measure of the tar is placed in a retort which it only one-third fills, so as not to spoil the distillate if there is much frothing during distillation. The retort should be supported on a cup-shaped piece of coarse wire gauze, placed in an aperture in a sheet-iron plate. Over the retort is placed a dome, made by removing the bottom from a tin can or bottle and cutting out a piece of the side to allow the neck of the retort to pass through. This contrivance confines the heat, and prevents the distillate or heavy vapour from falling back; indeed, without some such arrangement a satisfactory assay of coal-tar in glass is nearly impossible. The products obtained by the distillation are: (1) ammoniacal liquor; (2) total light oils; (3) creosote oil; (4) anthracene oils; and (5) pitch. In obtaining these fractions, the character of the distillate is amply sufficient to indicate the point at which the receiver should be changed. No thermometer is necessary, nor need any condensing arrangement be attached to the retort. A powerful bunsen should be used, as toward the close of the operation it is necessary to maintain the wire-gauze at a red heat. The ammoniacal liquor and naphtha are collected together in a graduated cylinder, which is changed as soon as a drop of the distillate sinks when collected in a test-tube of water. After standing, to allow perfect separation of the *ammoniacal liquor* and *light oils*, the volume of each is observed, and, if desired, the strength of the former can be ascertained in the usual way by distillation with lime and titration of the distillate. The quantity of light oils is too small for further fractionation.

The next fraction of the distillate consists of *creosote oil*. At first it will contain much naphthalene, and will probably solidify in white crystals on cooling, but afterward a more fluid distillate is obtained. At a still later stage a drop of the distillate collected on a cold steel spatula will be found to deposit amorphous solid matter of a yellow or greenish-yellow colour; the receiver is now again changed, the

fraction measured, and, if desired, assayed for phenol and naph-
thalene, as described in the section on "Creosote Oils." With many
tars this fraction is semi-solid, and must be measured while quite
warm.

The next fraction of the distillate is rich in anthracene, and not
unfrequently condenses in the neck of the retort as a yellow, waxy
substance, which may be melted out by the local application of a small
bunsen flame.

The collection of *anthracene oil* is complete when no more dis-
tillate can be obtained, and the pitch intumesces and gives off
heavy yellow fumes. The distilled fraction is then measured
and cooled thoroughly, and the resultant pasty mass pressed
between folds of blotting-paper, weighed, and assayed for real
anthracene by the anthraquinone test. The result is calculated
into *crude anthracene* at 30%, a standard which is generally adopted
by manufacturers.

When the distillation for anthracene oil is complete, the retort may
be allowed to cool, and when almost cold its body should be plunged
into cold water. This produces a rapid surface-cooling and shrinking
of the pitch from the glass; the latter may then be broken and removed
by gentle tapping, leaving the cake of *pitch* clean and ready for
weighing.

The following figures, communicated by B. Nickels, show the
results obtained by the assay of four representative samples of London
tar. The apparent excess is due to the tar having been measured and
the pitch weighed:

	A	B	C	D
Ammoniacal water	2.5	3.7	8.0	5.0
Total light oils	2.5	3.4	0.5	3.2
Carbolic and creosote·oils	21.3	17.0	23.0	20.0
Anthracene oils	17.0	17.0	13.0	13.0
Pitch (grm. per 100 c.c.)	59.4	60.0	58.0	62.0
	102.7	101.1	102.5	103.2
Pressed anthracene	4.0	......	1.15	......
Containing real anthracene	13.4%	......	25.68%	
=30% crude anthracene in tar	1.8	1.47	1.3	1.12

The following are typical analyses of present-day (1909) tars from London gas works using Durham coal.

	A	B
Ammoniacal liquor	3.9	3.1
Naphtha	1.63	1.56
Carbolic oil	11.87	12.00
Creosote oil	4.37	4.3
Anthracene oil	21.87	22.21
Pitch	53.65	54.44
Loss on distillation	2.71	2.39
	100.00	100.00

The reviser is indebted to Mr. Ernest F. Hooper for the foregoing figures, as also for the following analysis of tar obtained by distilling Ruhr coal in a Dessau vertical retort:

Water 1.5
Light oils .... 3.6 to 338° F.
Medium oils.........................15.5 to 446° F.
Heavy oils .... 11.6 to 518° F.
Anthracene oil ....30.0 to 716° F.
Pitch 37.0

Mr. C. C. Tutweiler, chemist of the United Gas Improvement Company of Philadelphia, has furnished the following copies of routine analyses of coal-tar, made from two typical American coals.

Sp gr., 1.227
Free carbon, 23.68% by wt. } Dry tar

Water, 13.2% by vol.

Dry tar   Distillation test

Crude products of distillation	Per cent. by volume	Per cent. by weight	Sp. gr.	Description of fractions
Light oils (below 338° F.)	....	....	....	
Middle oils (338°–518° F.)	17.8	14.41	0.993	Yellow oil and naphthalene
Anthracene oils (above 518° F.)	37.3	33.40	1.099	Med. red
Residuum	....	49.50	....	Hard, black, and porous
Total	55.1	97.31	....	

Sp. gr., 1.232.

Free carbon, 27.43% by wt. } Dry tar

Water, ——% by vol.

Dry tar   Distillation test

Crude products of distillation	Per cent. by volume	Per cent. by weight	Sp. gr.	Description of fractions
Light oils (below 338° F.).......	0.56	0.37	0.8240	Light green
Middle oils (338°–518° F.)	15.68	13.55	1.064	Red. green
Anthracene oils (above 518° F.)	29.23	26.34	1.110	Dark red brown
Residuum....................	....	55.91	....	Black and brittle
Total,....................	45.47	96.17		

Water is always determined by distillation. This may be done in round-bottom glass flasks of ample capacity, but the best form of still is probably one of spun copper with a head that is clamped in place by a screw. A bent glass tube or, preferably, a connection that gives a little space for the return of the vapours before coming to the tube going to the condenser is fitted to the head by means of a cork. The condenser is a straight glass tube running through a copper trough holding three or four liters of water, which can be heated to melt naphthalene that might otherwise obstruct the tube. The copper retort is heated by a ring burner that can be raised or lowered in position. Two or three hundred cubic centimetres of tar are weighed into the retort after thorough mixing of the sample by pouring from one can to another and stirred with the aid of a rod. A part of the water may separate in the sample can before carrying to the analyst, or it may be so intimately mixed with the tar that sampling is readily effected. In addition to the tar 50 to 75 c.c. of xylol or mixed coal-tar solvent free from water is added. It is perferable to add a distillate boiling above that of xyleme, so the mixed distillate with fractions next higher than xylene is preferable. After fastening on the cover and making it tight with gasket, moistened with a little melted pitch, etc., and connected with the condenser, the distillation is begun. The distillate is best caught in a receiver consisting of a tube about as thick as a burette, with a stop-cock at the bottom, and graduated from this point up to 20 c.c.

There is a widened portion holding about 100 c.c. This tube, as made for the Barrett Manufacturing Company, Phila., U. S. A., is fitted with a glass stopper at the top so that it can be used as an agitating tube for the sulphonation test according to Dean and Bateman

(U. S. Forest Service Circ. 112) and it could be used to estimate phenols in crude carbolic acids, etc. The amount of water in cubic centimetres as read from the receiver is divided by the cubic centimetres of tar taken, as calculated from the weight taken by sp. gr.

Sp. Gr.—This is best carried out by the method given on p. 95.

The methods of examining the fractions obtained in the first distillation of coal-tar will be described in the sections on "Commercial Benzols," "Naphthalene," "Anthracene," and "Creosote Oils."

COAL-TAR PITCH.

This is the residue remaining in the still after the first distillation of coal-tar, and usually amounts to about 2/3 of the weight of tar operated on. Its physical characters depend somewhat on the kind of coal distilled and the point at which the distillation was arrested. Thus, soft pitch is obtained if the process is stopped when the oils distilling have a sp. gr. of about 1.090, and hard pitch if it is continued until the sp. gr. of the products distilling reaches 1.120. In order to obtain a large yield of anthracene, the distillation is sometimes pushed as far as possible, and the residual hard pitch diluted with a certain proportion of creosote oil or anthracene oil, whereby a product of any requisite softness can be obtained. A compounded pitch of this sort will yield a notable quantity of liquid oils when distilled, and, possibly, naphthalene, which last is much objected to.

Soft pitch can be easily kneaded between the teeth, but moderately hard pitch with difficulty only, while hard pitch crushes to powder. Soft pitch is blacker and more lustrous than hard pitch, which often has a grayish tint and is somewhat porous. In the latter case it is partly coked, and is unfit for making patent fuel, for which pitch of but moderate hardness is preferred. The sp. gr. of hard pitch ranges from 1.275 to 1.300.

<div style="margin-left:2em">

Soft pitch   softens at 40° and melts at about 60°.
Moderately hard softens at 60° and melts at about 80°.
Hard   softens at 80° and melts at about 120°.

</div>

Contract notes for pitch intended for exportation to the Continent often stipulate that a sample is to "twist fairly after immersion for two minutes in water at 60°, but not under 55°; must contain at least 53% of volatile organic matter; and must be free from any extraneous matter, such as sand or grit."

The twisting point and m. p. of pitch are ascertained by F. G. Holmes by fixing several pieces of the sample (about 1/2 inch cube) on wires, by heating the ends of the wires sufficiently to press them into but not quite through the pitch, and suspending them, side by side with a thermometer, in a beaker containing 500 c.c. of water, which is heated at the rate of about 5° per minute. The pitch is taken out from time to time, and the twisting point taken as the temperature at which the fragment can be fairly twisted round several times. The m. p. is the temperature at which the pitch melts off the wire, avoiding premature dropping. The wires must be similar—copper wire of 16 imperial standard gauge is usually employed.

The proportion of volatile organic matter in pitch ranges from 47 to 64%. It is estimated by gradually heating 1 grm. (in some works, 5 grm.) of the carefully sampled and powdered pitch in a platinum crucible until distillation ceases. The operation should occupy about fifteen minutes, and must not be hurried, or the pitch may swell up and even boil over the sides of the crucible, leaving a very porous residue. A cover with a small aperture in the centre is then placed on the crucible, which is placed in a crucible-jacket and further heated for ten minutes over a powerful bunsen, and finally for ten minutes over a blast-flame. The residual *coke*, which should be dense and graphitoidal, is then weighed, and the volatile organic matter calculated from the loss. With care and attention to details the test gives constant results, but otherwise very discordant figures may be obtained. The coke may be burned and the proportion of ash ascertained if the presence of *sand* or *grit* is suspected.

Pitch testing is, however, in a very unsatisfactory condition, so much depending on the personal factor, especially in the twisting point test, and it is very desirable that the whole question should be investigated.

PITCH TESTS.

The reviser of this section is indebted to Mr. F. E. Dodge, chemical engineer of Philadelphia, for the following notes.

Melting Point.

Apparatus:

  (a)   Mould for making 1/2 in. cubes of pitch.
  (b)   Beaker 250 to 300 c.c. capacity; 2.5 in. diameter at the bottom. With 200 c.c. of water.

(c)   Wire for suspending pitch which is bent in the form of hook after the cube has been fastened upon it.

(d)   Bunsen burner adjusted so that it will raise the water 9° F. each minute.

Operation.—A 1/2 in. cube of the pitch is fastened upon a wire by heating the wire sufficiently to force it through the cube; after this is done, the wire is bent close to the cube into a right angle and suspended in the beaker of water so that the bottom of the cube is exactly 1 in. from the bottom of the beaker.

The water in the beaker should have a temperature of about 60° F., and in case of low m. p. or soft pitch, 5 minutes should be allowed before applying the heat.

The temperature of the water is taken by a thermometer suspended in the beaker with the bottom of the bulb on a level with the bottom of the cube of pitch.

The temperature is raised 9° F. each minute and the temperature when the pitch just touches the bottom of the beaker is considered the m. p.

Softening-point.—If the softening-point is also to be ascertained, a larger beaker and 500 c.c. of water is used, and several cubes of pitch are hung in the water. The temperature is raised at the same rate of speed, *i. e.*, 9° F. per minute. Cubes are removed and twisted from time to time, and when the cube can be twisted around 2 or 3 times without breaking, the softening-point is reached. The test may be continued until the m. p. is reached.

In case the pitch melts above 90 or 95° (194–203° F.), it will be necessary to use a solution of calcium chloride in water or brine, in which to take the m. p. Glycerin may also be used. It is necessary that the pitch have either a heavier or lighter sp. gr. than the solution used. In cases where the sp. gr. is lighter the pitch will rise in the solution, and when it just reaches to the surface is taken as the m. p.

Breaking-point.—A 1/2 in. cube of pitch is fastened to a copper plate by melting slightly so that it adheres firmly. It is then placed in tepid water and allowed to remain 5 minutes. The point of a knife blade is then slid along the plate till it touches the pitch, and then forcibly and slowly raise the point through the pitch. If the pitch is still soft, it will push its way through, but if the breaking-point is reached the pitch will scale off with conchoidal fracture. The tempera-

ture of the water is slowly lowered by the addition of cold water and allowing the pitch to stand for 5 minutes between trials.

The Slide Test.—A 1/2 in. moulded cube of pitch is placed on a grooved copper plate inclined at an angle of 30° and kept in an oven at the temperature of exactly 40° (104° F.) for 12 hours. The length of the stream of pitch is measured in inches, and is used for comparison of different pitches to be used for a given purpose. The grooved plate has several grooves and several samples are usually tested at the same time.

The Evaporation Test.—10 grm. of the pitch are heated in an air-bath for 7 hours at exactly 160° (320° F.) and the % loss noted.

Free Carbon Determination.—1 to 5 grm. of pitch are accurately weighed in a weighed extraction thimble, Schleichler and Schull, 80 x 22 mm., and first extracted with hot toluol (about 90°). Suspend the thimble in a beaker, so that it does not touch the bottom or sides, by passing a fine wire through the top of the thimble and pour in successive portions of toluol, but not into the thimble. After soaking for two hours in the toluol, the thimble is transferred to a Soxhlet extractor and suspended by the wire so that it does not touch the bottom and extracted with hot benzol, occasionally changing the solvent benzol, and continuing until the solvent becomes colourless, finally drying the thimble and weighing.

Melting- and Softening-point.—An alternate method is that used by Clifford Richardson for asphaltic materials. It is also used for pitches, for which it is quite suitable (see page 76).

The proximate composition of pitch is little understood. It always contains small quantities of the higher boiling tar oils, such as naphthalene, anthracene, chrysene, etc., but the bulk of it consists of fusible carbon compounds, of still higher b. p. (termed collectively "tar bitumen") and in addition, so-called "free carbon" is also present. This latter remains behind on successive extraction of the pitch with benzene, carbon disulphid, and alcohol, as an infusible black powder, resembling anthracite, but by no means consisting of elementary carbon. Thus, Behrens obtained from a pitch 23.54% of such a powder, containing 8.19% of hydrogen, and 0.4–0.9% of ash. The amount of this "free carbon" increases with the carbonisation temperature, so that the amount found in tar and pitch is now much higher than formerly, as much as 30% being sometimes found in tar, and over 40% in pitch.

The following analyses made by S. S. Sadtler show some of the differences between water gas pitch and coal-tar pitch.

	Water-gas pitch	Standard coal-tar pitch
Sp. gr.	1.21	1.29
Softening-point	107.3	106.8 F.
M. p...	147.2 F.	141.8 F.
Loss by evaporation at 329° F. during 7 hours.....	5.25%	2.51%
Percentage of free carbon	5.43%	28.80%
Distillate above 300° C........................	25%	29%
Green oil fraction	(liquid)	(semi-solid)
Extracted with petroleum ether	10.74%	7.55%

COKE-OVEN TAR.

The rapid spread of patent coke ovens with recovery of by-products has, of course, resulted in the production of very large quantities of coke-oven tars, and these tars show marked differences from gas-works tar. The ovens may be regarded as of two types—first, such as the beehive (from which tar is rarely obtained) and the Jameson, where air is admitted to the oven; and, second, those (Simon-Carvé, Otto-Hilgenstock, and many others) in which the oven is externally heated by gas and the access of air prevented as far as possible. Those of the first class yield tars very similar to those obtained from blast furnaces or by distillation of shale; they are usually lighter than water, contain little or no benzene, naphthalene, and anthracene, but considerable quantities of paraffins. The externally heated ovens, on the other hand, yield tars somewhat similar to those obtained from the gas works, and are examined and utilised in the same way. The temperatures in these retorts are high and the distillation lasting 24 to 30 hours, cracking takes place; consequently these tars are poor in light oils, but rich in both naphthalene and anthracene.

The following is a typical analysis of a tar obtained by distilling a Durham coking coal in Otto-Hilgenstock ovens:

The sp. gr. of the tar was 1.198 and it contained 10.5% of free carbon. 1,000 grm. distilled from a copper still gave the following fractions:

Ammoniacal liquor 2.4
Light oil (to 170°) 1.4
Carbolic oil (170°–230°) ....   8.0 (filtered and pressed gave 3.6 oil and 4.4 crude naphthalene.)
Creosote oil (230°–270°) ....   9.8 (of which 3.3 = oil, 6.5 crude naphthalene.)
Anthracene oil (270° and upward).. 24.8 (17.8 anthracene oil; 7.0 crude anthracene.)
Pitch ....'....................... 51.8
Loss 1.8
                               100.0

Examining the tars from various coke ovens using Durham coking coals, and taking 50 gallons of tar for each experiment, Mr. Ernest F. Hooper obtained the following figures (private communication):

	Simon-Carvé	Otto	Otto-Hilgenstock
Water............... ..	4.5	4.0	4.0
Naphtha	0.5	0.6	0.25
Light oils.............	1.0	1.5	1.75
Creosote oil	17.4	15.7	18.0
Heavy oil.............	18.6	13.7	10.δ
Pitch	58.0	63.0	66.0
	100.0	98.5	100.0

WATER-GAS TAR.

In many illuminating gas plants, particularly in the United States, a large portion of the gas is made from carburetted water gas—water gas, to which, while incandescent, a stream of petroleum oil is injected. The tar from this form of gas-making is quite useful. Benzol, toluol, etc., naphthalene, creosote oil and pitch or coke are obtained. It is distinguishable from coal-tar in that its sp. gr. is very low, it has little if any free carbon, practically no tar acids, and the anthracene oils are mostly liquid at the ordinary temperature. The following works analyses are furnished by Mr. C. C. Tutweiler.

Sp. gr.,   1.092
Free carbon,   trace

Crude products of distillation	% by volume	% by weight	Sp. gr.,	Description of fractions
Light oils (below 338° F.)	1.39	1.09	.8557	Colourless
Middle oils (338°–518° F.)	16.84	14.87	.9585	Greenish-yellow
Anthracene oils (above 518° F.)..	59.23	57.28	1.056	Deep red
Residuum.....................	.....	24.72	.....	Black and brittle
Total	77.46	97.96	.....	

Sp. gr.,   1.083   Water, 4.25% by vol.
Free carbon,   0.73%

Crude products of distillation	% by volume	% by weight	Sp. gr.	Description of Fractions
Light oils (below 338° F.)	3.97	3.68	.9255	Yellow
Middle oils (338°–518° F.)	28.44	28.27	.9939	Yellow
Anthracene oils (above 518° F.)..	36.62	39.66	1.0831	Dark red green fluorescence
Residuum	.....	24.10	.....	Hard, black, porous
Total	69.03	95.61	.....	

BITUMENS.

By S. S. SADTLER.

Mineral products consisting essentially of a complex mixture of hydrocarbons are found in numerous localities, and under very varied circumstances. These products, of which petroleum may be regarded as a type, occur in all parts of the world, and, like coal, are not confined to any one geological formation.

The natural hydrocarbons present every variety of aggregation, from the state of gas, as evolved from coal and petroleum, through the conditions of a thin mobile liquid, like the naphtha of Persia, the viscous tar of Rangoon, the elaterite or mineral rubber of Derbyshire, the wax-like ozokerite of Galicia, to the brittle, pitch-like asphalt of Trinidad.

The origin of the bitumens or mineral hydrocarbons is, in many cases, obscure. The subject has been treated in an able and exhaustive report by S. F. Peckham,[1] and has been discussed by many writers. Products more or less similar to petroleum and asphalt have been obtained by distilling complex animal and vegetable matter out of contact of air. All the evidence tends to show that the natural bitumens are derived from various sources. Peckham has reviewed the question (*Amer. Jour. Sci.*, Nov., 1894) and reiterated his earlier statement. Engler (Petroleum, 2, (1907) 849, 912, 964, and 1021) has recently contributed a full discussion on the subject of the formation of petroleum in which all points are considered, including the bearing of the optical activity of some oils. His belief at this time is that it has come largely from cellulose.

A more recent article by M. P. Delvilde (Mon. sci. du Quesneville, May, 1907) reviews the inorganic theories of Humbolt (1804), Berthelot (1866), Sabatier and Senderens (Compt. rend., **134**, (1902),

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[1] *Report on the Production, Technology, and Uses of Petroleum and its Products* to the Hon. C. W. Seton, Department of the Interior, U. S. America. Peckham concludes that all bitumens have, in their present condition, originally been derived from animal or vegetable remains, but that the manner of their derivation has not been uniform.

1187) and contrasts them with the organic theories. This article upholds the inorganic theories. The weight of evidence seems, however, to be with the organic hypothesis. The chief grounds perhaps for this view are the fossil remains occurring in strata in which petroleum is native, the presence of nitrogenous compounds and the optical activity of many oils. In mineralogy the term bitumen includes all natural substances which contain notable proportions of hydrocarbons. Peckham proposes the following classification:

Solid,	Asphalt.
Semi-solid,	Maltha.
Liquid,	Petroleum.
Gaseous,	Natural gas.

The consideration of the different varieties of coal is beyond the scope of this treatise.

Petroleum.   Rock Oil.   Mineral Oil.

French—Pétrole. *German*—Erdöl. *Spanish*—Petrólea.

Petroleum is a natural oily liquid occurring in the earth at very varied depths, and in a great many localities.   It is not confined to any particular geological formation.   Thus, the petroleum of the great Pennsylvania field is derived from the Devonian and Carboniferous limestone formations, while that of California and Russia is found in tertiary rocks.   Petroleum may not be indigenous to the strata in which it is found; in some instances it has undergone distillation or been forced from one stratum to another by the pressure of gas and water. An exact definition of the term Petroleum can hardly be given.   The more viscous varieties may be nearly black in colour and contain such amounts of oxygenated constituents and sulphur (both free and combined) that make it partly asphaltic in its nature and hard to distinguish from a maltha.   Commercial usage alone will draw the line between a heavy black petroleum and thin black maltha.

Petroleum has now been found or its presence definitely indicated in almost every country in the world.   It has now been obtained, however, on a considerable scale in the Caucasus, on the shores of the Caspian Sea, and smaller quantities are produced in Canada, Austria-Hungary, Germany, Roumania, and other localities, but the largest quantity is obtained from the United States.   The last source so overshadows all others, from a commercial point of view, that the following description applies chiefly to that product:

Crude natural petroleum is an oily liquid, varying in density from

0.73 to 0.97, the Pennsylvania product ranging between 0.79 and 0.83. It has a characteristic odour, sometimes, but by no means invariably, disagreeable; its colour varies from straw-yellow to brownish-black. Its coefficient of expansion varies considerably with its sp. gr., as is shown by the following table:

Sp. gr. at 15°	Expansion-coefficient for 1°
Under .700	.00090
.700 to .750	.00085
.750 to .800	.00080
.800 to .815	.00070
over .815	.00065

On a stock of 1,000,000 barrels of petroleum, the shrinkage in winter amounts to 7,000 to 10,000 barrels.

Petroleum is insoluble in water, and but slightly soluble in alcohol, but it is miscible in all proportions with chloroform, ether, carbon disulphide, and hydrocarbons. It mixes readily with ordinary fixed oils, castor oil being an exception (Vol. 2, page 163). All varieties are combustible, burning with a luminous, more or less smoky, flame.

Chemical Composition of Petroleum.—Chemically, crude petroleum consists of a mixture of a considerable number of hydrocarbons with small quantities of sulphur and sulphuretted, nitrogenised, and oxygenised bodies.

The nitrogen in crude petroleums and paraffin oil is given thus by Beilby (*J. Soc. Chem. Ind.*, 1891, **10, 120**):

Scotch shale oil from retorts	1.160%
Scotch petroleum or ozokerite	0.296%
American petroleum residuum	0.080%
Baku petroleum residuum	0.050%
Baku petroleum	0.050%
Galician ozokerite	0.188%
Scotch basic tar	3.900%
American residuum tar	0.716%
Scotch crude still coke	3.200%
American crude still coke	0.375%

Prof. C. F. Mabery (*J. Soc. Chem. Ind.*, 1900, **19,** 504) examined a number of samples of California petroleums and found the nitrogen percentage to vary between 0.23 and 0.88 as determined by Kjeldahl's method. Because of the high molecular weight of the nitrogenous substances, they would amount to probably 10 to 20% of the weight of the oils. These constituents were fractionally separated and their composition as pyridine homologues was established. The bases seem to

exist as esters, but are easily set free. The more the bitumens have been exposed, the less nitrogen is found. Very little is found in asphalts.

According to Kast and Lagai (*Ding. Poly. Jour.*, 1892, **284,** 69), all crude petroleums, except that from Tegernsee, contain sulphur in amounts varying from 0.136 to 1.87%. Mabery and Smith have investigated the nature of the sulphur compounds in California oils and find that they are in the form of alkyl sulphides; thiophen and mercaptans are absent.

Mabery and Quayle (*J. Soc. Chem. Ind.*, 1900, **19,** 505) investigated crude Canadian oils and isolated a series of alkyl sulphur compounds by distilling at a pressure of 50 mm.

Richardson and Wallace (*J. Soc. Chem. Ind.* 1901, **20,** 690) have found free sulphur to be the form in which a large part if not nearly all of the sulphur in Texas (Beaumont oil) exists. Some hydrogen sulphide is dissolved in the oil and a large amount is formed if the oil is heated as in distillation, when it comes off in considerable quantities.

Petroleum is variable in composition, and more or less volatile and mobile according to its content of bitumen and solid bodies. In general, it contains about 85% of carbon and 15% of hydrogen, but its elementary composition gives no idea of the variety of hydrocarbons contained in it. In brief, the constituents of petroleum present the following varieties of character:

(*a*) Their volatility is very different, for they extend from gases of very low b. p. to solids which boil at high temperatures (370° and 450°).

(*b*) The volatility of the constituents is usually inversely as their sp. gr., the lightest oils being the most volatile.

(*c*) The inflammability is a function of the volatility, the more volatile constituents taking fire on approach of a flame at ordinary temperatures, while the denser and less volatile oils require to be heated considerably before they can be inflamed or made to give off inflammable vapours.

The hydrocarbons of petroleum belong to several series, the paraffins largely predominating in American petroleum, while members of other series are present in relatively large amount in the petroleum of other regions.

Pennsylvania petroleum has been most completely studied. A complete series of paraffins, from CH_4 to $C_{16}H_{34}$, has been obtained from it; and the solid members, $C_{25}H_{52}$, $C_{27}H_{56}$, and $C_{30}H_{62}$, are also

present, especially in the oils from the Bradford (Penna.) district. Iso-paraffins, as well as the normal forms, exist in American petroleum. The paraffins from CH_4 to C_4H_{10} are gaseous at ordinary tempera-tures, and hence escape in admixture with hydrogen from petroleum wells, or when the petroleum is stored or gently heated. The mem-bers from C_5H_{12} to $C_{15}H_{32}$ constitute the greater part of the liquid portion of American petroleum, one of the most characteristic con-stituents being hexane. Mabery (*Proc. Am. Acad. Arts and Sciences*, **32**, 121, and **37**, 565) has isolated the hydrocarbons of Pennsylvania petroleum as well as most of the other oils from important localities. The olefines from $C_{10}H_{20}$ to $C_{12}H_{24}$ have been isolated by Warren from American petroleum, and doubtless other of the higher members of the series are present. Gaseous olefines also occur. Naphthenes similar to those characteristic of Russian petroleum are also present. Benzene and its homologues exist in traces in American petroleum, and among the less volatile constituents anthracene, chrysene, pyrene, fluoranthrene, and thallene exist in small quantity.

Natural gas from the Pennsylvania wells has been found to contain from 40 to 94% (largely the higher percentages) of methane, CH_4, with smaller proportions of hydrogen and ethane, CH_6, and traces of higher homologues. Small proportions of olefines are also present. On the other hand, the liquid obtained by J. J. Coleman, by the action of cold and pressure on the gases produced in the distillation of bitumi-nous shale, consisted chiefly of butylene, C_4H_8, pentene, C_5H_{10}, and hexene, C_6H_{12}. Natural gas is employed for manufacturing and household purposes in many of the Middle and Western States of the United States. F. C. Phillips (*Proc. Engin. Soc. Western Pennsylvania*, Dec., 1898), has found from one to nearly 3% of nitrogen in natural gas.

Canadian petroleum contains various hydrocarbons of the paraffin and olefine series, and is richer in aromatic compounds and poorer in gaseous paraffins than the Pennsylvania product. Mabery (*Proc. Am. Acad. Arts and Sciences*, **32**, 156 (1897), and **40**, 334 (1904)) has shown that the low b. p. hydrocarbons belong to the paraffin series and those above 196° to the olefine series. It contains a notable quantity of sulphur compounds and traces of benzene and nitrogenous basic oils. It yields about 3% of solid paraffin.

Californian petroleum contains, as shown by Mabery (*Proc. Am. Acad. Arts and Sciences*, **36**, 256 (1901)), benzene hydrides, naphthenes,

and aromatic hydrocarbons. Sulphur compounds with a notable amount of the esters of nitrogenous basic oils have been shown to be present by Peckham and others.

Ohio petroleum is intermediate in properties between Caucasian and Pennsylvania oils, and contains the following: Methane, 2 butanes, pentane, isopentane, hexanes, heptanes, octane, nonane. These form less than 10% of the oil. The crude oil contains a large amount of sulphur compounds. Aromatic hydrocarbons are present in very small amount. The sulphur compounds have a tendency to collect in the higher fractions. Mabery has also carefully studied these oils (*Proc. Am. Acad. Arts and Sciences*, **40**, 323, 1904).

Russian petroleum has acquired considerable commercial importance. It is chiefly obtained in the neighborhood of Baku on the Caspian Sea, but is also found in other parts of the Caucasus. A fraction of given b. p. has a higher density than a similar fraction of American petroleum or Scotch shale oil, and the viscosity is more readily decreased by heat. It usually yields no solid paraffin.

This petroleum is scientifically interesting from its peculiar composition. Beilstein and Kurbatow could not obtain any products of constant b. p., even after nine distillations, nor were they able to extract any benzenoid hydrocarbons by treatment with fuming nitric acid nor any olefines with bromine. Their researches, as extended by Schützenberger and Ionine, and by Markownikoff and Oglobini, have shown that Caucasian petroleum consists chiefly of a mixture of naphthenes, having the general formula C_nH_{2n}. These are isomeric with the ephylenes, and with the benzene hexahydrides (so-called paraffenes, $C_nH_{2n-6}H_6$), obtained synthetically by Wreden. With the exception of the hydrocarbon $C_{13}H_{26}$, all the naphthenes from C_8H_{16} to $C_{15}H_{30}$ have been separated from Caucasian petroleum. They boil at somewhat lower temperatures than the isomeric olefine and the normal paraffins containing the same number of carbon atoms, and at approximately the same temperature, as the synthetically prepared paraffenes; but the sp. gr. of the Caucasian hydrocarbons are notably greater than those of the isologous paraffins from American petroleum. Thus, while normal octane, C_8H_{18}, boils at 124° and has a sp. gr. of 0.7188 at 0°, octonaphthene, C_8H_{16}, boils at 119° and has a sp. gr. of 0.7714. Similarly, $C_{12}H_{26}$ boils at 202° and has a sp. gr. of 0.7655, while $C_{12}H_{24}$ boils at 196° and has a sp. gr. of 0.8027 at 17°,

The naphthenes do not form nitro-derivatives, and resemble the

paraffins in not yielding additive compounds and in being convertible into chlorinated derivatives from which alcohols are obtainable. When oxidised, the naphthenes form oxidation-products, or are converted into higher isologues.

The higher boiling portions of Caucasian petroleum probably contain hydrocarbons of the olefine and higher series, while 10% of the petroleum consists of aromatic hydrocarbons belonging to known series, and also a series of hydrocarbons isomeric with styrolene and its isologues. These compounds form brominated derivatives, but no additive compounds; their aromatic character is exhibited in the formation of nitro- and sulpho-derivatives. A petroleum from near Tiflis, examined by Beilstein and Kurbatow (*Jour. Chem. Soc.*, **40,** 1020), yielded a fraction of lower b. p. containing the paraffins C_4H_{10} to C_7H_{16}, with a little benzene and toluene. By treating the fraction of a Caucasian petroleum boiling between 180° and 200° with fuming sulphuric acid, Markownikoff and Oglobini found that various sulphonic acids were formed, while the hydrocarbons of the formula C_nH_{2n} were left unchanged. Isomerides of cymene, metamethyl-propylbenzene, and probably durene, were present. The 240° to 250° fraction contained a modification of propylnaphthalene ($C_{13}H_{14}$), then $C_{12}H_{14}$ and $C_{11}H_{14}$ (the last probably belonging to the cinnamene series), and finally $C_{15}H_{30}$ (? $C_{15}H_{10}$). The petroleum also contains neutral and acid oxygenated bodies. A petroleum examined by Markownikoff yielded a fraction boiling between 220° and 230°, which contained 5.25% of oxygen.

The investigation of Russian petroleum is very difficult, owing to the facility with which the constituents break up into other bodies on distillation, especially during the latter part of the process. When passed through an iron tube heated to bright redness, Caucasian petroleum yields an abundant deposit of carbon, which soon chokes the tube, the metal itself being strongly corroded. The volatile products consist largely of benzene and its homologues, with naphthalene and anthracene. This reaction has been utilized for the production of benzene and anthracene from Russian petroleum.

Galician petroleum, according to Lachowicz, contains a number of paraffins and also aromatic hydrocarbons. Pawlewski found in a petroleum from Kleczany about 2% of aromatic hydrocarbons, consisting chiefly of benzene and *p*-xylene. The fraction boiling between 97° and 100° consists chiefly of heptane with some toluene

hexahydride, but the presence of xylene hexahydride was not established. The first six fractions obtained by distilling the crude petroleum on the large scale are not acted on by bromine, but the seventh and higher fractions absorb bromine with evolution of heat. Hence it is probable that olefines do not pre-exist in the petroleum, but are formed during the distillation by the decomposition of paraffins. Hell and Meidinger have isolated from Wallachian petroleum an acid forming alkali salts resembling soft soap. Other homologous acids are probably present.

Galician petroleums, according to R. Zologiecki and H. Klarfeld (*Chem. Zeit.*, **31**, 1155–6, 1170–2), have been found to give the strongest indications of having optically active constituents. Consideration of the optical activity in petroleum is mainly given because of its bearing on the question of its origin. It had been held originally by Engler and others that it had come from animal remains, while the discovery of the optical properties of certain petroleums has given strong reasons for the belief that it has had its source from vegetable as well as from animal remains.

Hanoverian petroleum, according to C. Engler, contains hydrocarbons both of the paraffin and olefine series, besides notable quantities of aromatic hydrocarbons (*e. g.*, pseudocumene, mesitylene, and probably hexahydrometaxylene). Sulphur compounds are also present.

Rangoon tar is a heavy variety of petroleum, of a semi-solid consistency, owing to the presence of about 40% of solid paraffin. By fractional distillation, Warren and Storer proved the presence of the paraffins from C_7H_{16} to C_9H_{20}, olefines from C_9H_{18} to $C_{13}H_{26}$, besides xylene, cumene, and naphthalene.

The composition of petroleums from other sources has been but imperfectly ascertained. The behaviour of some of them on distillation is described later.

DISTILLATION OF PETROLEUM.

The method of treating crude petroleum for the manufacture of commercial products varies considerably with the character of the crude article and the practice of the works, but it is always essentially a process of fractional distillation, sometimes supplemented by a decomposing action in the still caused by the hot vapours of the oil

striking the colder walls of the stills which condenses it, and as it falls back in the hot liquid it is "cracked" or split up into lower boiling constituents and correspondingly heavier and high boiling bodies rich in carbon. To avoid this "cracking" the tops of the stills are covered so as to condense as little as possible, or a more efficient method, namely, that of driving the vapours over with superheated steam, is followed. The character and proportion of the various products obtained depend largely on the nature and source of the oil and the details of the mode of treatment, which is capable of considerable variation in detail. As a rule, the lighter and more volatile portions are fractionated into a number of products, known commercially as cymogene, rhigolene, gasolene, naphtha, and benzin; but in many cases the proximate separation of the products of the distillation of crude petroleum is less complete, only three principal products being made—namely, naphtha, kerosene, and lubricating oil. By the present system of manufacture, "cracking" of the heavier oils (see under "Kerosene"), about 75% of burning oil, flashing at 20° (68° F.) by Abel's test, may be obtained from some crude American petroleums. The yield of higher-class oils (such as would pass English inspection) is smaller, and of "water-white oil" only from 12 to 20% is obtained. The proportion of naphtha obtainable from American oil varies from 9 to 18%, according to the age of the oil-producing territory.

Caucasian petroleum yields very different proportions, the proportion of burning oil flashing at 32° and of 0.821 sp. gr. being only about 27%; but a much larger percentage of oil of lower flashing-point or higher sp. gr. can be obtained. B. Redwood (*J. Soc. Chem. Ind.*, 1884, **3**, 74), who gives the above figures, also states that the Caspian Company manufactures three qualities of the burning oil, of the following characters:

Quality	Sp. gr.	Flash-point	Yield, %
1	0.815	30°	20
2	0.820	25°	33
3	0.821 to 0.822	22°	38

The following table of products from 100 gallons of Russian petroleum is from information furnished by the Ragosine Company.

Products	Sp. gr.	Gallons
"Benzin"	0.725	1
"Gasolene" or heavy benzin	0.775	3
Kerosene	0.822	27
Pyronaphtha (flash-point 132°, open test)	0.858	12
Lubricating oil	0.890–.905	27
Cylinder oil	0.915	5
Vaseline (not a direct product)	0.925	1
Residuum and loss	....	24
		100

The heavier lubricating oils or "oleonaphthas" of the Ragosine Company range in density from 0.905 to 0.920, and have low freezing-points.

The fractions of the crude petroleum obtained by distillation are purified by treatment with a limited quantity of strong sulphuric acid, and then washed with sodium hydroxide, and finally with water. In some works they are then redistilled over sodium hydroxide. In Canada the burning oil is treated with a solution of litharge in sodium hydroxide to remove sulphur-compounds, and in Ohio copper oxide has been used (Frasch process). Texas crude is distilled about the same as Pennsylvania oil, and the hydrogen sulphide that is evolved is disposed of by partial combustion to sulphur or else spray condensers are used and the hydrogen sulphide carried off in the water. Texas oil is chiefly distilled for gas oil and lubricating "residuums."

The following is an outline of the usual process of petroleum distillation as conducted in America: The oil is heated in large stills holding from 600 to 1,200 barrels. The more volatile portions soon come over; they are either burnt as gas or, for limited use, condensed by artificial cold and pressure. The liquids thus obtained are known as "cymogene" and "rhigolene." After these, products condensible by cold water are obtained, the first portions having a sp. gr. of 0.636, the product becoming heavier as the distillation proceeds. (The distillate obtained in this part of the operation is usually again distilled, when it yields "gasolene," "naphtha," and "benzin.") When the liquid passing over acquires a sp. gr. of 0.725 to 0.750—according to the works' custom—the stream is diverted from the "naphtha" tank to the "kerosene" receiver, where it is collected until its sp. gr. reaches 0.840 to 0.845. The residue is then transferred to other stills, and gen-

erally to other works, where it is distilled to dryness to obtain lubricating oils and paraffin. The residue in the still is combustible with difficulty, but is used as fuel. If the operation be arrested before actual coking occurs, the residue has the characters of thick tar. The purification and fractionation of the first products are conducted in much the same manner as with shale oil.

On the Caspian Sea the distillation of the petroleum is conducted as a continuous process, a stream of oil flowing through the entire series of 14 or 16 stills heated to successively higher temperatures. This method is peculiarly suited for the treatment of Russian petroleum, since it yields comparatively little burning oil, and the residue is almost as fluid as the crude oil. The distillate is collected in 2 fractions: gasoline and kerosene, the gasoline is re-distilled with steam giving a gasoline with gravity of 0.750, sp.gr., and the residue is pumped in with the main kerosene fraction, giving kerosene of 0.825. The residue has a density of 0.903, and yields on distillation about 35% of lubricating oil and 10 of "solar oil" (sp. gr. 0.860, flashing-point 105°), the remainder being commonly used as fuel. Attempts have been made to employ *astatki* (residuum) for the production of benzols and anthracene by subjecting it to a full red heat. Baku petroleum contains little or no solid hydrocarbons, but the oil obtained on the other side of the Caspian yields as much as 6%.

Assay of Crude Petroleum.—According to a definition adopted by the New York Produce Exchange in 1879, "crude petroleum shall be understood to be pure natural oil, neither steamed nor treated, free from water, sediment, or any adulteration, of the gravity of 43° to 48° Baumé" (=0.8092 to 0.7865 sp. gr.). The usual range in the sp. gr. of the New York crude oil is between 0.790 and 0.800. Each parcel is usually a mixed product from a number of wells.

The *water* and *sediment* are usually estimated by mixing the sample with an equal quantity of petroleum spirit, free from water, and keeping the mixture at 49° (=120° F.) in a graduated glass vessel for at least six hours, after which the liquid is allowed to cool and settle for a period of not less than 2 hours for light grade oils, increasing to 18 hours for the heaviest qualities. The estimation of water is preferably made by distillation and measuring the water that comes over in thin-bore graduated tubes.

The sp. gr. is generally taken by means of the hydrometer, although for accurate work, such as is requisite when oil is measured in bulk and

settled for on a basis of weight, the sp. gr. bottle or pyknometer is pref-
erable. The Westphal balance is also preferable to the use of the
hydrometer.

Besides the test for water and the determination of the sp. gr., the
ordinary characters relied on as commercial tests of the quality of crude
American petroleum are: Its odour and colour, its feel when rubbed be-
tween the fingers, and the percentage of naphtha yielded on fractional
distillation. The crude oil of the New York market will generally
furnish from 12 to 15% of naphtha of 0.700 sp. gr., and the proportion
should not exceed 17%. It will yield, in addition, from 9 to 12% of
benzin of 0.730 sp. gr. and about 60% of burning oil at 0.795 sp. gr.
The residue contains a quantity of dry paraffin scale equal to about
2.5 % of the crude oil.

Fuller's Earth Test.—Recently Day and Gilpin (*J. Ind. and Eng.
Chem.*, **1**, 449–55, 1909) have developed a method of fractional
separation of petroleum oils by means of clay (fuller's earth). They
used for this work tin tubes 5 ft. long and 1.25 in. in diameter,
closed at the bottom with corks, upon the sides of which were grooves
to admit the oil. These tubes were packed with fuller's earth, a little
at a time, with a ramrod. They were then placed in vessels con-
taining petroleum and the air in the tubes was removed by a pump
to facilitate the diffusion. After the oil had nearly reached the top
of the tubes the clay was removed in sections and treated with water to
displace the oil. All the oil from one section of the tube is of the same
colour, irrespective of whether it is the first or the last oil to come off
when water is added. The sections vary, however, as to sp. gr.,
the first oil collected being the heaviest.

Besides the selective action of the clay upon the paraffin hydrocar-
bons themselves, certain constituents of petroleum are held back by
the clay with great readiness. Such substances are asphalt and the
sulphur compounds found in Texas petroleum.

Unsaturated hydrocarbons do not diffuse as rapidly through the
clay as the saturated. Substances in colloidal suspension in general
seem to be held back most readily.

Assay of Crude Petroleum by Distillation.—The method of Engler
has been perhaps most generally used. The distillation flask (Fig. 1)
is shown with the measurements in centimeters. Flasks that do not
come up closely to these measurements should be rejected. The bulb
of the thermometer is just below the side delivery tube. In making

a distillation, wire gauze is used at first as a protection from the flame, but after the lightest fractions have come over it is removed and the distillation carried on with the naked flame. The heat is so regulated that from 2 to 2 1/2 c.c. of distillate pass over per minute. As soon as the requisite temperature (150° for the first fraction) is reached, the
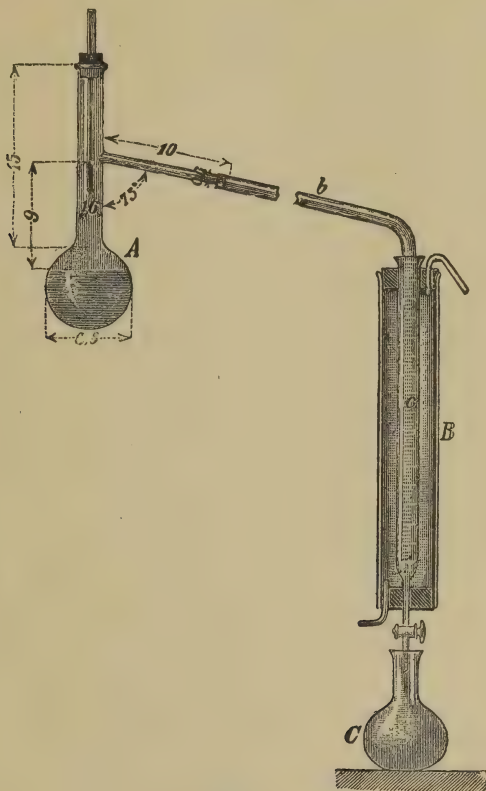
FIG. 1.

burner is withdrawn until the temperature has fallen 20°. The oil is then reheated to the b. p. and allowed to cool as before. This is repeated until no more distillate comes over at this point. The same procedure is gone through with at the next point of separation of fractions.

According to the practice followed by Engler, each fraction boiling at

intervals of 25° is caught separately and then the different portions, after measurement of quantity, are added together to see what are the characters of the different cuts, naphtha, kerosene, neutral and lubricating oils. With oils consisting essentially of paraffin hydrocarbons, such as Pennsylvania and Galician oils, the kerosene cut is taken from 150° to 300°. In the case of oils of the naphthene series, such as Baku oil, the kerosene fraction is taken between the limits of 150° and 285°. Higher boiling oils cause an excessive charring of the wicks. The Engler method will probably be superseded by the method of Ubbelohde.

The Bucharest Congress on Petroleum adopted the method of Dr. Leo. Ubbelohde, in which he distils the samples in an Engler flask, but does not cool and reheat several times at 150° and 300°, as he found the small amounts of vapour would not be sufficient to give the correct thermometer reading. He distils at a uniform rate of 2 drops per second and by comparison with distillations using dephlegmators he observed that he obtained more reliable results than by Engler's method. He did not think the use of dephlegmators was as necessary for kerosene as they were for benzin. In using this method the bulb and flame must be protected from air draughts.

Another form of distilling apparatus is that of Regnault, which is much used in France. It consists of a copper retort, passing into a metallic condenser, which terminate above and below in narrow tubes. The condenser is fitted into a cylinder, containing water. The apparatus is compact and convenient to use.

Dephlegmators are sometimes used to secure a more complete separation of the constituents of petroleum. While it is true that it does serve this purpose if well constructed, it is probably better for the sake of uniformity to adhere to the method of Engler or Ubbelohde, just described. Uniform results can be obtained with them in the hands of different operators. Dephlegmators differ in construction, and differences in operation have large influence upon the results obtained with their use.

Sp. gr. tests of fractions are made by means of a pyknometer or Sprengel tube (if the amount is small). A small thermometer plummet is often used to examine distillates, with good results.

Some useful hints on the assay of crude petroleum have been published by Nawratil, who has examined a number of Galician petroleums. He distils 500 c.c. in a glass retort. The distillate collected

below 150° is regarded as light oils or naphtha, that from 150° to 300° as burning oil, and that from 300° to 400° as heavy oils. The sp. gr. of the original samples (18) ranged from 0.902 (Harklowa) to 0.799 (Kenczany), and the proportions of the several fractions showed similar variations. The light oils varied from 43.5 to 3.4%, the 150° to 300° fraction from 45.4 to 29.2%, and the heavy oils from 56.7 to 22.8%.

Determination of the Calorific Value.—While some authorities recommend the calculation from the results of an ultimate analysis, it is probably best to make a direct determination in a standard form of calorimeter, such as the Mahler bomb. The operation of this instrument is detailed in various works on fuels.

Of course, full directions for use are supplied with each instrument.

The calorimeter devised by S. W. Parr can be used, if it is properly standardised by comparison with some hydrocarbons of similar constitution. This calorimeter is more suitable, however, for coal. The Rawle (*J. Soc. Chem. Ind.*, 1907, **26,** 665) instrument has been gaining favour in England, as being specially adapted for liquid fuels. A cut accompanies the article.

To extract *solid paraffin* from crude petroleum, Sadtler mixes the oil with several times its volume of ether, and places the liquid in a freezing mixture, when "almost all the dissolved paraffin will separate, and can be filtered off." For other than Pennsylvania crudes precaution must be taken to separate out any asphaltic bodies or they would contaminate the paraffins (see Holde-Richardson method, page 104).

The *flashing point* of petroleum is an indication of considerable importance, but is more especially connected with the examination of refined petroleum or kerosene, under which head the subject is fully discussed.

Estimation of Sulphur.—The standard method for the estimation of sulphur in crude petroleum has been, and probably still is, the method of Carius. It consists in oxidizing the entire sample of oil with fuming nitric acid in sealed tubes of hard glass at temperatures around 200°. This method is often found very troublesome due to the bursting of tubes. Several other methods give practically identical results if properly carried out, but at the same time the method of Carius will always be the standard method. A brief description of the method is given on page 85.

The only other method that can be considered practically as reliable
as that of Carius is the combustion of the oil in a bomb calorimeter.
Methods that are more suited for rapid routine work are that of Ma-
bery; an adaptation of the Burton-Sauer method, and one the reviser
of this section has found useful in certain cases.   The Mabery method
(*Proc. Amer. Acad.*, **31**, 1 (1896)) consists in burning the substance con-
tained in a porcelain boat in a current of air or oxygen, which enters
the combustion tube containing the boat by a small tube of hard glass
which is continued beyond the boat to a restriction about midway in
the tube.   Air also enters the combustion tube through another tube
passing in a little beyond the double-bored stopper that carries the
longer tube.   This air carries oil vapours, which come from the oil due
to heat applied carefully below the boat, to the restriction where they
meet the main body of air.   Beyond the restriction the tube is heated
to redness.   The sulphur is burned to sulphur trioxide and is ab-
sorbed in a dilute sodium hydrate solution contained in a large U-tube
partly filled with glass beads.   It is rather difficult to get a proper ad-
justment of rates of flow, temperatures, etc., unless a person has worked
with the method quite a while, and the reviser found that more ready
combustion could be obtained if a wad of platinised asbestos were
placed ahead of the constriction or, better yet, between two of them,
leaving space an inch in length.   This catalyser causes an intensely hot
spot, locally, where the oil vapours and the air meet, and the reviser was
able in that way to burn Texas oils, which otherwise seemed to be very
difficult to burn by the ordinary Mabery-Burton-Sauer method.   This
difficulty seemed to be due to the force of gas due to the rather sudden
liberation of hydrogen sulphide from the action of sulphur on some of
the hydrocarbons, when the proper temperature was reached.

    A different method brought out by the "Reviser" (*J. Amer. Chem.
Soc.* (1905), **27**, 1188), known as the double crucible method, is found
very useful for determining sulphur in crude oils and residuums which
contain sulphur in excess of 1%.   It has been found satisfactory for
analysing Texas crudes, and compares favourably with the Carius
method.

    The crucible is shown in Fig. 2.[1]   The substance is first weighed into
the inner crucible, which is placed open end up on the balance pan.
About 1 grm. of sulphur compound containing 1% sulphur is taken.

    Enough Eschka mixture is then put in to absorb the substance, if

[1] Cut reproduced from *J. Amer. Chem. Soc.*, with permission.

a liquid, or mixed with it in any case, and then filled to the top with moderate tamping.

Freshly ignited white asbestos (a) is then put around the raised portion of the bottom of the outer crucible to keep the two crucibles from being in actual contact. It is then lowered over the inner crucible and then both crucibles inverted. Eschka mixture is then put in between the crucibles. The outer crucible is then put through a hole in a piece of thin but firm asbestos board so that very little, if any, of the sides can be exposed to the direct action of the flame.
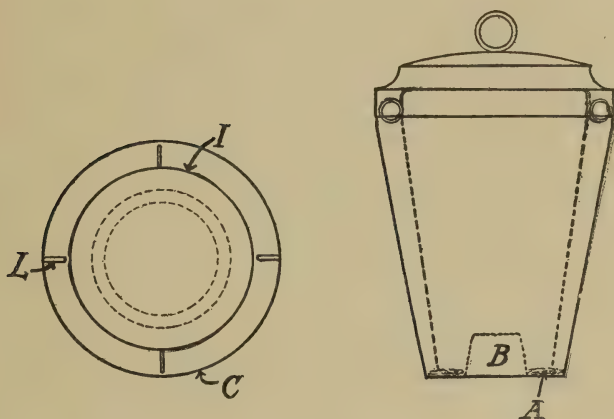
Fig. 2.

The outer crucible is made with straight sides like an inverted truncated cone.

A very small pointed flame of a Bunsen burner is now used so that the flame is chiefly in the indentation on the bottom (b). If gases do not come off from the crucible in three to five minutes with this flame, the heat is increased, and when no more odour is noticeable the crucible is placed in a piece of asbestos having a larger hole, so that half of the crucible may become red-hot and is kept so for 10 minutes. The flame is then withdrawn, and when cool the inner crucible is carefully raised and tapped, so that its contents are dropped into the outer one, when the carbon is burned out with a shield of asbestos to protect the contents from the sulphur gases of the flame.

The contents of the crucibles are then washed into a beaker.   Brom-ine is added to oxidise sulphites, etc., the solution is filtered, acidified, and precipitated with barium chloride as in the case of determinations of sulphur in coal.

Asphaltic matters in crude petroleum are determined by D. Holde (Lunge's Chem-tech. Untersuchungsmethoden, Berlin, 1900, 3, 7), with benzin and with alcohol-ether as follows:

1. Benzin method is carried out by taking 1.5 to 3.0 grm. of the oil in a litre flask, of colourless glass, and adding 300 to 500 c.c. of benzin of the lightest grade (gasoline 88°, Baumé) and shaking well. It is allowed to stand at least 1 day.   The supernatant solution is then decanted through a filter and finally the precipitated asphaltic matter.   The filter is thoroughly washed with gasoline and then the asphalt dissolved in sufficient hot benzol into a tared flask.   After evaporating the benzol, the residue is weighed and considered as asphalt.

2. A somewhat different result is usually obtained by using alcohol-ether (4–3) as a precipitant.   1 to 2 grm. of the oil are taken and 40 c.c. of the alcohol-ether mixture are added in a stoppered flask and well shaken.   It is then allowed to stand 2 or 3 days.

The asphaltic material is filtered as in the case of the gasoline method and the asphalt washed with alcohol-ether (4–3) both on the filter and in the flask.   It is then dissolved with hot benzol and weighed.

OZOKERITE.

This substance, known also as cerasin, cerite, or mineral wax, usually occurs in the neighborhood of petroleum springs, and in as-sociation with bituminous sandstone, clay-schist, gypsum, and common salt.   Though not very abundant, ozokerite occurs in many parts of the globe, the most remarkable and best-known deposit being that in the miocene rocks of Galicia, on the slopes of the Carpathian Moun-tains, and also on the Wallachian side of the range.   It is also worked on the island of Tscheleken in the Caspian and at Swatoi-Astrow, near Aphesron, where a variety called *neftgil* is found.   It exists also in Turkestan, and a valuable deposit has been found in Utah.   Its com-mercial interest is chiefly as a source of cerasin, though liquid hydro-carbons are also obtained by the distillation of the inferior kinds.

According to Brannt ("Petroleum and Its Products," 400), Sauer-landt has found ozokerite to contain:

Volatile hydrocarbons.
Paraffins melting at from 60° to 70°.
Waxy resins, } Oxygenated.
Bituminous resins, }
Coke.

Crude ozokerite varies much in appearance. The finest varieties are transparent, of a pure yellow or greenish colour, and can easily be kneaded between the fingers. Crude Galician ozokerite is a scaly or waxy substance, with a resinous fracture. It is usually brittle, but as hard as beeswax. It becomes negatively electric by friction and exhales an aromatic odour. According to Lach (*Chem. Zeit.*, **13,** 831), the so-called ozokerite from Colorado does not yield cerasin, but is suitable for paraffin making. It begins to distil at 360°, and yields 90% paraffin and oil and about 5% of residuum. Caucasian ozokerite yields about 58% of a second-quality cerasin.

Inferior kinds of Galician ozokerite are black and soft, or hard, with a fibrous structure and conchoidal fracture, varying in colour from yellow ("butter-stone") to black. Some pieces are as hard as gypsum, and are dichroic, the transmitted light being a pure yellow, and the re-flected dark green. The m. p. is very variable, ranging from 58° to 100°. The raw ozokerite occurring on the island of Tscheleken, in the Caspian Sea, is a brownish-black sticky mass, almost entirely soluble in boiling benzene. On extracting it with ether, the oily portion and colouring matter are dissolved, leaving a hard residue. On boiling this with acetic ether, the paraffin is dissolved, and by repeated treat-ment with animal charcoal, etc., may be obtained in lustrous crystals, melting constantly at 79°, and containing 85.10 of carbon and 14.57 of hydrogen (Beilstein and Wiegand, *J. Chem. Soc.*, **44,** 1073).

Ozokerite is separated from the gangue by being melted, and, after being pressed, is treated with alkali and filtered through fine animal charcoal. Frequently both acid and alkali are used in the purification of ozokerite; fuller's earth and magnesium silicate have been substituted for the charcoal. The charcoal used is preferably the fine carbonaceous residue produced in the manufacture of potassium ferrocyanide (cyanide black). The purification of ozokerite with sulphuric acid is attended with considerable loss, owing to the action of the acid on the oxygenated bodies present. Peritz obtained from 75 to 82% of crystallised paraffin from Boryslaw ozokerite, and 9 **to**

13% of light oils. Ozokerite refined in England yields nearly 70% of white paraffin. The purified substance constitutes *cerasin*, which name should be confined to the solid paraffin obtained without distillation. Inferior ozokerite is usually distilled with superheated steam, when it yields paraffin wax, lubricating oil, naphtha. Galician ozokerite yields on distillation about 25% of petroleum, 21 of lubricating oil, and 36 of solid paraffin. A higher yield might doubtless be obtained by improved manipulation. B. Redwood (*J. Soc. Arts*, xxxiv, 886) gives the products as 5% of gaseous hydrocarbons, 3% of naphtha, 6 of semi-solid "ozokerin," 12 of soft paraffin (melting at 44° to 46°), distilled ozokerite (melting at 61°), and a black waxy residue. The following are the products obtained by the distillation of Caspian ozokerite (*neft-gil*), according to Grabowski: 2 to 8% of benzin, 15 to 20% of naphtha, 15 to 20% of heavy oils, 36 to 50% of solid paraffin, and 10 to 20% of coke.

Sometimes the products are less carefully differentiated, the chief being:

30 to 40% of benzin of 0.73 sp. gr., and
50 to 76% of solid paraffin melting at from 60° to 70°.

The crude ozokerite is worked up for cerasin, paraffin being extracted from the residue, which then forms "ozokerite pitch." In distilling for paraffin, a burning oil comes over at 150°, the fraction 200°–300° consisting of a mixture of heavy oil and paraffin, and being worked up for the latter or for vaseline, while the chief yield of paraffin comes from the fraction 300°–350°. The average yield of the various distillation products is, at Boryslaw: Light oil (up to 150°), 6%; heavy oil (150°–300°), 32%; paraffin, about 55%.

Assay of Crude Ozokerite.—According to B. Lach (*Chem. Zeit.*, 1885, 905), for the valuation of crude ozokerite 100 grm. of the sample should be treated with 20 grm. of fuming sulphuric acid in a tared basin. The mixture is heated to 170° to 180°, and continuously stirred till all sulphur dioxide has escaped. On reweighing the basin, the loss is said to represent the volatile constituents—namely, *petroleum* and *water*. No allowance appears to be made for the loss due to the formation of sulphur dioxide and possible volatilization of sulphuric anhydride. Probably a better plan would be to dilute the mixture, and separate and weigh the paraffin. Lach further directs that another quantity of 100 grm. of the sample should be treated with 10 grm. of the carbonaceous residue from the manufacture of potassium

ferrocyanide, which has been previously dried at 140°. A tenth part of the mixture (11 grm.) is then weighed into a tared paper thimble, and extracted with petroleum spirit, boiling between 60° and 80°. The wax is estimated from the loss, or recovered by evaporating the solvent. This result would probably be high while the first method of Lach would undoubtedly be low, therefore it seems that the suggested modification of the first method would be the best to follow.

Refined ozokerite or cerasin usually melts between 61° and 78°, is quite odourless and colourless, and has a waxy section. A variety manufactured in Frankfort-on-the-Oder is said to melt at 83°, and to be so hard as scarcely to yield to the finger-nail. Cerasin possesses the general characters of paraffin wax. The commercial samples are sometimes artifically coloured.

Cerasin may be distinguished from bleached beeswax by its lower sp. gr. and by its resistance to alcoholic potash, no trace of saponifiable matter being present. In mixture with beeswax, cerasin may be detected and approximately estimated by the methods given in Vol. 2, page 258.

Ozokerite vaseline is obtained by allowing melted ozokerite to pass through 12 to 15 filters of animal charcoal, or through double that number if a perfectly colourless product be required. The mass is then treated, for 3 to 4 hours, with superheated steam (250°). About 25 to 30% of product is obtained.

ASPHALT.

Asphaltum. Mineral Pitch.

German—Erdpech. *French*—Asphalte. *Spanish*—Asfalto.

Under the term asphalt is included a considerable number of natural products, consisting largely of compounds of carbon and hydrogen mixed with substances containing oxygen, nitrogen, and sulphur, also some mineral matter. A portion of this mineral matter sometimes exists in combination with the oxidised or sulphurised substances, forming compounds analogous to those produced by resins. Such compounds may dissolve in the liquids employed for the fractionation of the asphalt in analysis, and thus error arise from computing the loss by solution as due entirely to bituminous matter.

Prof. S. F. Peckham describes asphalt as follows: "The natural bitumen, which is known as asphalt, is composed, as far as we have

been able to learn, of unsaturated hydrocarbons and their sulphur derivatives with a small amount of nitrogenous constituents. Asphalt may, therefore, be defined as any hard bitumen composed of unsaturated hydrocarbons and their derivatives, which melts on the application of heat to a viscous liquid; while a maltha or soft asphalt may be defined as a soft bitumen which, on heating, leaves an asphalt, or becomes by natural causes converted intó one. The line between the two classes cannot be sharply drawn.

"Asphalts are distinguished by the large amount of sulphur they contain, and it is to its presence that many of the important characteristics and perhaps, in part, the origin of this form of bitumen is due. The soft asphalts or malthas contain much less sulphur than the harder ones, if the former are rich in sulphur, they are then in a transition stage and would eventually become hard."

Deposits of asphalt occur in all parts of the world; each locality yields a material more or less distinct in character. Of late years much attention has been paid to the analysis of asphalt, especially in the United States, owing to the discovery of new and important local deposits and the extensive introduction of asphalt-paving in American cities. This paving is often merely an asphaltic mixture, inferior to the rock-asphalt employed in Europe. Even mixtures of coal-tar pitch, and petroleum residuum without true asphalt have been used.

Natural asphalts exhibit wide differences in composition. Some forms (rock-asphalts) consist of limestones or sandstones saturated with bituminous matter. In other cases but little mineral matter is present, and in still other cases the mineral matter is abundant, but is simply mixed with the bituminous material and does not produce a rock-asphalt.

Blake (*Trans. Amer. Inst. Min. Eng.*, 1889–90, 563) gives the following list of the principal localities of the several types of asphalt:

Mixed with calcium carbonate ...Seyssel; Val de Travers; Lobsann; Illinois.
Mixed with sandstone...........California; Kentucky; Utah.
Mixed with earthy matter (clay)..Trinidad; Venezuela; Cuba; California; Utah.
Bituminous schists ....Canada; Kentucky; California; West Virginia.

Some asphalts, such as Trinidad and Bermudez, are submitted to a refining process before being marketed. This consists in heating the crude material in large kettles to not over 200°, by which much water

and some volatile matters are removed, portions of the earthy materials, principally clay and sand, allowed to settle, and some of the non-bituminous organic substances collect as a scum and may be removed. Petroleum residuum may be added during this operation, which will, of course, increase the amount of bituminous matter, especially that soluble in petroleum spirit, and produce a strongly fluorescent solution.

Although asphalts have been used for a long period in engineering work, the first scientific investigation seems to have been made by Boussingault (*Ann. d. Chim.*, **64** (1837), 141; also *Compt. rend.*, Meeting of Sept. 16, 1836), who, in 1836, examined a viscous material from Pechelbronn. He tried several solvents, but relied more upon a process of distillation in an oil-bath, by which he obtained a liquid to which he gave the name "pétrolène." He assigned to this a composition of $C_{80}H_{64}$ (C=6), pointing out that it was isomeric with oil of turpentine. The non-volatile portion he designated "asphaltène," and assigned to it the formula $C_{80}H_{64}O_6$ (C=6,O=8), but recognised that oxidation had occurred during the distillation, and that therefore the proportion of asphaltène obtained was in excess of the true amount. From an ultimate analysis of the material, he computed that the proportions of pétrolène and asphaltène were about 85.4 and 14.8, respectively. He also made a brief examination of the asphalt of Coxitambo.

Boussingault's methods are not now used, but by a curious misapplication, the terms petrolene and asphaltene have been applied to the products obtained by the use of solvents. Efforts have been made to establish standards for judging of the value of an asphalt for engineering uses by means of these methods. Carbon disulphide is sometimes used to determine the total bitumen, all organic matter left undissolved being regarded as non-bituminous. For the fractionation of the bituminous matter, petroleum spirit, ethyl ether, acetone, boiling oil of turpentine, chloroform, and benzene have been employed. Usually the portion soluble in petroleum spirit, ether, or acetone is called petrolene, and that insoluble in either of these liquids, but dissolved by boiling turpentine and cold chloroform, is designated as asphaltene. The organic matter insoluble in any of these solvents, and also in carbon disulphide, is considered as non-bituminous, and is thought to be objectionable if present in notable proportion, rendering the paving mixtures liable to rot in the gutters. It has also been stated that clay will tend to produce disintegration. Many engineers have adopted

or accepted limits of the proportion of petrolene to asphaltene in asphalts intended for paving purposes. Thus, Tillson (Trans. Amer. Soc. Civ. Engin., 1897, 214) accepts any refined asphalt that contains from 50 to 60% of bitumen of which not more than 25 to 30% is asphaltene. This does not apply to rock-asphalts, which may contain less than 10% of bitumen. Petrolene is regarded as acting as a solvent on the asphaltene.

The calcareous asphalts have a deep brown or black colour, and break without any sign of cleavage, the fracture being earthy and very similar to chocolate both in colour and appearance. When long exposed to the air, the surface acquires the appearance of ordinary limestone, but on fracturing the specimen the interior will be found unchanged. The proportion of bitumen cannot be judged from the appearance.

The average sp. gr. of rock-asphalt is about 2.23. It is very hard and sonorous when cold, and may be broken with a hammer. In summer it is softened by blows to a kind of paste, and at 50° to 60° falls to powder. Some rock-asphalts, such as that of Lobsann, contain a volatile oil which renders them greasy. This oil may be removed by distillation, after which the asphalt is fit for use.

Good rock-asphalt has a fine and homogeneous grain, and no particle of white limestone is visible. The rock is often streaked, while other samples contain crystals of calcite of considerable size, but impregnated with bitumen like the matrix, which is an important characteristic. Bad qualities are imperfectly impregnated, or contain so small a proportion of bitumen as to render it difficult to work them. The presence of clay spoils the homogeneous nature of the asphalt, and causes fissures.

When intended to be used for paving, the Val de Travers, Seyssel, and other rock-asphalts are often melted with a certain proportion of rich native asphalt, such as Trinidad pitch, the product being called "mastic." The mastic is often mixed with a further proportion of bitumen, residuum, shale oil, and mineral matter.

Composition of Rock-asphalts.—The following data are compiled from various sources, as indicated. The detailed statement of the mineral ingredients is given somewhat vaguely in some of the reports, but the principal ingredients will serve for comparison. The loss at or about 100° is designated by some analysts as water, but it may include bituminous matters:

Source	Loss at 90° C	Soluble in carbon di-sulphide	Calcium Carbonate	Magnesium Carbonate	Sand or clay	Sulphur	Authority
Ragusa.....................	....	9.72	88.75	.....	.....	....	Tillson.[1]
Seyssel....................	....	8.15	91.70	.....	.....	....	Tillson.[1]
Seyssel....................	190	8.00	89.55	0.10	0.25	....	Orton.[2]
Val de Travers.............	....	7.20	.....	.....	.....	....	Tillson.[1]
Val de Travers.............	....	12.00	.....	.....	.....	....	Tillson.[1]
Val de Travers.............	0.50	10.10	87.95	0.30	.....	....	Orton.[2]
Limmer....................	....	14.30	67.00	.....	17.52	....	Sadtler.[3]
Limmer....................	....	8.26	56.50	27.01	4.98	....	Orton.[2]
Vorwohle..................	....	5.37	90.80	.....	2.55	....	Sadtler.[3]
Lobsann...................	3.40	11.90	69.00	0.30	3.05	5.00[6]	Orton.[1]
Forens..	0.20	2.25	97.00	0.70	.....	....	Orton.[1]
California.................	2.50	20.20	3.00	.....	74.00	....	Hilgard.[4]
California.................	0.33	15.13	.....	.....	83.4c[7]	....	Linton.[5]
Kentucky..................	....	5.76	.....	.....	94.22[7]	....	Linton.[5]
Turrelite (Texas)........	....	12.05	87.94[7]	.....	.....	....	Linton.[5]

Composition of Soft Asphalts.—The natural asphalts other than the true rock-asphalts show great differences in composition, both as regards the proximate constituents and the nature and amount of mineral matter. The following table includes the more important forms. The total bituminous matter has usually been estimated by solution in carbon disulphide, or by successive extraction with petroleum spirit, boiling turpentine, and chloroform. The mineral matter is mostly a ferruginous clay. The ash, obtained by burning a known weight of the asphalt, does not represent exactly the mineral matter in the original material, but the difference is not important, as at present the details of its composition have no practical value. A group of analyses of Trinidad asphalt are here given as reported by Clifford Richardson (*J. Soc. Chem. Ind.*, **17**, 13 (1898).

CRUDE LAKE PITCH.

	Percentage soluble in			Percentage of total bitumen only soluble in			
	Petroleum ether	Boiling spirits turpentine	Chloroform	Total bitumen	Petroleum ether	Boiling spirits turpentine	Chloroform
Average	35.2	12.4	5.2	52.8	66.8	23.3	9.9

[1] Trans. Amer. Soc. Civ. Engin., 1897. [2] Rep. to Geol. Survey of Ky. (data from German sources). [3] *Ind. Org. Chem.* [4] Ann. Rep. State Mineral. of Calif., 1890; average of fourteen samples. [5] *J. A. C. S.*, 1894 and 1896. [6] Present as iron sulphide. [7] Total mineral matter; the details of composition are not given, except that Turrelite is stated to consist largely of sea-shells cemented into a mass by the bitumen.

CRUDE LAND PITCH.

Average	33.3	11.9	6.5	51.7	64.7	23.0	12.3

AVERAGE COMPOSITION OF TRINIDAD LAKE PITCH FROM THE BORING.

54.66	35.90	9.44	31.53	57.67

AVERAGE COMPOSITION OF LAKE PITCH, DRIED (IN VACUO), KEARNEY COLLECTION.

Bitumen-soluble CS², %	Mineral matter, %	Organic, not soluble., %	Bitumen-soluble petroleum naphtha, %	Total bitumen-soluble, %
Average 54.25	36.51	9.24	35.41	65.27

AVERAGE COMPOSITION OF LAND PITCH, DRIED (IN VACUO), KEARNEY COLLECTION.
EIGHT SPECIMENS FROM LOT C., NEAR THE LAKE.

Average	54.03	36.49	9.48	33.02	61.11

FOUR SPECIMENS FROM CROWN LAND LOTS ADJOINING C.

Average	58.81	36.62	9.57	32.29	60.01

COMPARATIVE COMPOSITION OF 1894 SAMPLES.

	Bitumen	Organic insoluble	Mineral inorganic
Lake, 2 ft. below surface	54.92	9.72	35.46
Land	52.36	11.24	36.40

	Bitumen soluble in naptha	Total bitumen soluble in naptha.
Lake, 2 ft. below surface	31.72	57.79
Land	29.02	55.43

ANALYSES FROM OTHER LOCALITIES.

Source	Soluble in carbon disulphide	Mineral matters	Non-bituminous organic matter	Authority
Grahamite, Va............	100.00	....	....	Linton.[1]
Bermudez..............	94.75	3.65	1.60	Richardson.[2]
Bermudez..............	98.52	0.50	0.98	Richardson.[2]
Bermudez..............	91.88	1.67	6.45	Richardson.[2]
California maltha.......	98.26	1.74	....	Tillson.[3]
California Kern Co.......	93.20	5.77	0.54	Tillson.[3]
Gilsonite, Utah..........	100.00	0.10	....	Day.[4]
Trinidad—Lake..........	52.97	36.10	10.96	Linton.[1]
Trinidad—Land.........	52.57	38.88	11.52	Linton.[1]

Adulterations of Asphalt and Asphaltic Mixtures.—Pure asphalt is much employed in the manufacture of black varnishes and japans and for other similar purposes. It is not unfrequently mixed with or substituted by *coal-tar pitch* and other artificial products, which render it quite unfit for some of its most important uses.

Asphalt for varnish-making should be entirely (or with the exception of 4 or 5% of earthy matters) soluble in carbon disulphide, chloroform, high-boiling coal-tar naphtha, and oil of turpentine. It is also said to be insoluble in alcohol or a mixture of equal parts of alcohol and chloroform. It should break with a conchoidal fracture and brilliant resinous lustre, the streak and powder being of a bright brown. Asphalt should not flow or lose shape like wood-tar pitch when left on a plane surface, and an angular fragment or chip should retain its shape and the sharpness of its angles in boiling water, and only begin to melt at about 150°. Asphalt adulterated with coal-tar pitch has a much less brilliant fracture-surface, and an adamantine or metallic rather than a resinous lustre. When fused at as low a temperature as possible, the adulterated asphalt has a granular pasty appearance and feel, instead of being smooth and homogeneous, and will not draw out into even and transparent brown threads like pure asphalt.[5]

The following figures, due to E. Davies (*Pharm. Jour.*, [3], **14,** 394), show the behaviour of certain natural asphalts, rock-asphalts, and their substitutes, with petroleum spirit. The proportions of sulphur and mineral matter are also recorded.

[1] *J. Soc. Chem. Ind.*, 1896, 275. [2] Contrib. from Lab. of Barber Asphalt Paving Co., Nov., (1898). [3] Trans. Amer. Soc. Civ. Engin., 1897. [4] *Jour. Frank. Inst.*, Sept., 1895.
[5] The characters of asphalt fitted for varnish-making given in the text are taken from Spon's *Encyclopædia*. They apply to refined asphalt.

For these analyses, 5 grm. of the finely-divided sample were digested for 1 hour with 50 c.c. of petroleum spirit of 0.70 sp. gr., and the mixture frequently agitated. The liquid was then boiled for a short time, decanted, and the residue boiled with another quantity of 25 c.c. of petroleum spirit. This treatment was repeated 8 or 10 times, till the exhaustion was complete.

Material	Ash	Action of petroleum spirit		Proportion soluble for 100 of organic matter	Sulphur	
		Soluble	Insoluble		Per 100 of material	Per 100 of organic matter
Val de Travers asphalt.......	90.24	9.76	none	100.00	.41	4.20
Fine Syrian asphalt. ...	.68	48.16	51.16	48.49	6.13	6.19
Low Syrian asphalt..........	2.64	49.68	47.68	51.02	5.65	5.80
Trinidad pitch..............	37.76	36.24	26.00	58.22	3.47	5.58
American asphalt...........	.60	65.64	33.70	66.03	.62	......
American asphalt...........	.26	63.62	36.12	63.78	.85	......
Stearin pitch..............	5.50	71.05	23.45	75.18	.04	......
Stockholm pitch..........	.84	91.46	7.70	92.23	.01	......
Rosin pitch...............	.58	86.94	12.48	87.45	.26	......
Coal-tar-pitch.............	.20	24.44	75.36	24.29	.69	......
Coal-tar pitch.............	1.06	18.70	80.74	18.90	.41	......
Coal-tar pitch.............	.48	15.86	83.66	15.94	.59	......

Of these samples, those of American asphalt were evidently manufactured and not natural products. They were probably petroleum pitch, and were black, brittle substances, having a conchoidal fracture and black streak. They differed from stearin pitch in their brittleness and the proportion of sulphur. The Stockholm pitch was black, too soft to powder, and very easily soluble in petroleum spirit. The rosin pitch had a conchoidal fracture, and gave a brown powder. The different proportions of matter soluble in petroleum spirit present in the samples of coal-tar pitch were no doubt due to the extent to which the respective distillations had been carried.

For the distinction between natural asphalt and coal-tar pitch reliance has sometimes been placed on the fluorescence of the petroleum-spirit solution when coal-tar products are present, but some crude asphalts also produce fluorescence and refined asphalt may contain petroleum residuum. Durand-Claye suggested the following test: The sample is digested in carbon disulphide, filtered, the filtrate evaporated to dryness, and the residue heated until it is hard and brittle after cooling: About 0.1 grm. is shaken for a few minutes with 5 c.c. of fuming sulphuric acid in a stoppered tube, the mixture allowed to stand for

24 hours, and then 10 c.c. of water added, drop by drop, with constant stirring, after which the liquid is filtered through paper. Natural bitumens will give a colourless or faintly coloured solution, but coal-tar pitch will give a dark brown. If the conditions of the test are uniform, approximate quantitative comparison of samples may be made. The following comparisons were made in Allen's laboratory:

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Rock asphalt............................Faintly colored.
Trinidad asphalt........................Slight brown.
Petroleum pitch  .......................No color.
Shale-oil pitch  .......................Hair brown.
Coal-tar pitch  ........................Very dark brown.
Bone pitch  ............................Very dark brown.
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According to Durand-Claye, 8 grm. of the sample are shaken with 5 c.c. of benzin in a closed glass vessel until dissolved. A few drops of the filtered solution are then diluted with 5 c.c. benzin and mixed with an equal volume of alcohol (85°, Gay-Lussac). The yellow or yellowish-brown colouration of the alcoholic layer gives an indication of the presence of tar distillation products. Even on dissolving in benzin some indication can be obtained, since native asphalt dissolves with a pure brown colour, while tar products give a strongly yellowish-green fluorescence.

To detect the presence of coal-tar pitch in asphalt, a small amount may be heated in a crucible. In this way coal-tar pitch may be distinguished from natural asphalt by its disagreeable, bituminous odour. Another very definite test for coal-tar pitch is due to the fact that it always contains free carbon in contradistinction to asphalt. Natural asphalts present a uniform brownish appearance when a very little is melted on a hot microscope slide and examined by a microscope. The free carbon in coal-tar pitch may be seen suspended in the bituminous matter that otherwise would look much like the asphalt.

Asphalt-paving Mixtures.—Many asphalts are unsuited for use in street-paving unless mixed with tempering materials. Practice, in American cities especially, has led to the selection of special proportions of petroleum residuum, sand, or stone-dust, and pulverized limestone. As a guide to the composition of these mixtures the official specifications of two large cities and some engineering notes are given. The Philadelphia specifications are in part based on the results of an examination made some years ago (Report of experts (Sadtler, Leffmann, and Lewis) selected by Citizens' Municipal Association and

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the Trades' League of Philadelphia, 1894), but agree in the main with those of most American cities.

Philadelphia, 1894.—If natural rock-asphalt is used for the wearing surface, it shall be natural bituminous limestone rock. From the Sicilian mines at Ragusa or the Catania mines, equal in quality and composition to that mined by the United Limmer and Vorwohle Rock Asphalt Company, Limited. From the Swiss mines of Val de Travers, equal in quality and composition to that mined by the Neufchatel Rock Asphalt Company, Limited. From the French mines at Seyssel, equal in quality and composition to that mined by Compagnie Générale des Asphalte de France in the proportions of 4 parts of the Sicilian Rock to 1 of the Seyssel or Vorwohle Rock.

If refined asphalt is used for the wearing surface, it shall be composed of the best quality of refined Trinidad or Bermudez asphalt, obtained from the so-called pitch or asphalt lake on the Island of Trinidad or from Bermudez, South America, or other asphalt which in quality and durability shall be equal to the standard of the Lake Trinidad or B .mudez, heavy petroleum residuum oil, fine sand, fine stone-dust, fine powder of calcium carbonate. The asphalt must be refined and as far as possible freed from organic and mineral matter and volatile oil, and should contain at least 60% of bituminous matter soluble in carbon disulphide; the residuum oil must be free from coke and other impurities, of a sp. gr. of 18 or 22 Baumé, and withstand a fire test of 250° F. The refined asphalt and residuum oil will be mixed in the following proportions by weight: asphalt 100, petroleum 16 to 22.

The asphaltic cement made in the manner above described will be mixed with other materials in the following proportion by weight, viz.:

Asphaltic cement	13 to 16
Sand	58 to 63
Stone-dust	23 to 28
Pulverised limestone	5 to 3

Complete specifications for making asphalt pavements including the foundations are rather lengthy, and the scope of this work only permits including the asphaltic layers themselves. Very full treatment of the entire subject can be obtained from a report of the commissioners of Account of the City of New York on Asphalt Paving, Feb. 3, 1904, and by consulting "The Modern Asphalt Pavement," by

Clifford Richardson, New York, 1905. The following is a portion of the specification suggested on pages 408–410 of the latter work.

Definition.—The pavement proper shall consist of a binder course . . . in. in thickness and a wearing surface . . . in. in thickness, equal in composition to the pavement mixture hereafter described.

Binder Course.—Stone.—The binder shall be composed of suitable clean broken stone passing a 1 1/4 in. screen, not more than 5% of which shall pass a No. 10 screen.

Asphaltic Cement.—The stone shall be heated in suitable appliances, not higher than 300° F., and then thoroughly mixed by machinery with asphaltic cement equivalent in composition to that hereinafter set forth, in such proportion as will cover the stone with a glossy coat and without any excess of asphaltic cement.

Laying.—The binder must be hauled to the work and spread while hot upon the foundation to such thickness that, after being immediately compacted by rolling, its average depth shall be . . . in., and its upper surface shall be approximately parallel to the surface of the pavement to be laid. Upon this binder course shall be laid the wearing surface of pavement proper.

No traffic, except such as may be required in depositing the surface mixture, or in otherwise prosecuting the work, shall be allowed on the binder course.

Pavement Mixture.—The pavement mixture for the wearing surface shall be composed of:

      (a) Asphaltic cement (refined asphalt and flux).
      (b) Sand of satisfactory grading and grain.
      (c) Filler, consisting of finely powdered mineral matter.

Refined Asphalt.—The asphalt employed in the preparation of the asphaltic cement for use in the asphalt surface mixture shall be a solid native bitumen obtained from some native deposit, and which has been in use in the paving industry for at least 5 years. It shall be so refined as to be in every respect uniform, of a character recognized as being suitable for the production of a satisfactory asphaltic cement and in all respects satisfactory to the city engineer.

Flux.—The oil used as a flux in the manufacture of the asphaltic cement shall be the residue from any satisfactory petroleum from which the lighter oils have been removed by the distillation without cracking, and having a sp. gr. of from 17° to 20° Baumé. It shall not

flash below 325° F. (New York State closed oil tester), and shall not volatilise more than 5% on heating for 7 hours at 325° F.

Asphaltic Cement.—The refined asphalt and flux, of character corresponding to that described in the foregoing paragraphs, shall be combined as follows for the preparation of the asphaltic cement.

To the melted asphalt, at a temperature of not over 350° F., the flux, after being heated to about 200° F., is to be added in such proportions as to produce an asphaltic cement having a consistency, as indicated by the Bowen penetration machine, of from 60 to 75° F. While the oil is being added agitation shall be maintained by means of an air blast or live steam, and shall be continued until the asphaltic cement is homogeneous. The agitation shall be continued for at least 3 hours, during which time the temperature shall be maintained at from 300 to 325° F. Should the finished cement not prove of proper consistency, it shall be modified by the addition of further oil or melted asphalt as may be necessary.

The asphaltic cement while in use must be thoroughly agitated. Samples of the same, and of the materials from which it has been prepared, shall be supplied to the city engineer when required.

Sand.—The sand to be used shall consist of hard grains, of satisfactory surface and shape, not containing more than 1% of clay or loam. On sifting, the whole shall pass a 10-mesh screen, 15% shall pass an 80-mesh screen, and at least 7% shall pass a 100-mesh screen.

Filler.—The filler shall be powdered mineral matter of such a degree of fineness that the whole of it shall pass a 50-mesh screen, and least 66% a 200-mesh screen.

Combining Materials.—The materials complying with the above specifications shall be mixed in proportions by weight, depending upon their character. The percentage of matter soluble in carbon bisulphide in any pavement shall not be less than 9.5 nor more than 12.0%.

The sand and the asphaltic cement will be heated separately to approximately 340° to 380° F. for the former, and 325° F. for the latter. The stone dust shall be mixed, while cold, with the hot sand. The asphaltic cement will then be mixed with the sand and stone dust, at the required temperature and in the proper proportion in a suitable apparatus, so as to effect a thoroughly homogeneous mixture.

Laying the Pavement.—The above mixture shall be hauled to the

streets in trucks properly protected from radiation by tarpaulin at a temperature of not less than 250° F. and spread upon the binder to such a depth as will assure an average thickness of . . . in. after ultimate compression. This compression will be attained by first smoothing the surface with a hand-roller, or light steam-roller, after which hydraulic cement or stone dust shall be swept over it, when the rolling will be continued with a steam-roller until the surface is properly compacted.

The specifications recommended in the Report of the Commissioners of Accounts of New York City differs chiefly from the above in that the proportions of "flux" and refined asphalt are not governed by a penetration test, but by a limitation as to proportions which shall not exceed 25 parts by weight of "flux" and 100 parts refined asphalt.

R. B. Stanton (*Trans. Amer. Soc. Civ. Engin.*, 1896, 73) used for reservoir-lining in California 4 parts best refined California asphalt and 1 part crude petroleum without sand; he also used broken stone, 2 inches and under, including all fine material. Trautwine employed at Philadelphia, for reservoir lining, 4 parts of Bermudez asphalt and 1 part of a liquid California asphalt.

Penetration machines or penetrometers are used for determining the consistency of asphalts and asphaltic cements. The machines that have been devised for this purpose are the Bowen, the Kenyon, and the New York Testing Laboratory Penetrometers.

Bowen's tester consists of a needle suspended on a level arm connected with a thread that moves a pointer on a dial. The depth to which the needle sinks will depend on the hardness of the asphalt. The apparatus is much used, but two machines will give concordant results only when constructed and operated exactly alike. Dow has devised a more elaborate apparatus, in which a needle penetrates by a direct weight without friction.

Analytical Methods for Asphalts.

The following methods on pages 70 to 73 are the official methods of the Society of Testing Materials (U. S. A.), and, as far as they go, are standard. As so many additional tests are given by Clifford Richardson, his methods are given in full, even duplicating in some measure those of the society.

Drying the Sample and Preparing it for Analysis.—It was decided, owing to the great variety of conditions met with in bituminous compounds, that it is impossible to specify any one method of drying that would be satisfactory in every case. It is therefore supposed that the material for analysis has been previously dried, either in the laboratory or in the process of refining or manufacture, and that water, if present, exists only as moisture in the hygroscopic form.

The material to be analysed, if hard and brittle, is ground and spread in a thin layer in a suitable dish (iron or nickel will answer every purpose) and kept at a temperature of 125° for 1 hour. In the case of paving mixtures and road materials, where it is not desirable to crush the rock or sand grains, a lump may be placed in the drying oven until it is thoroughly heated through, when it can be crushed down into a thin layer and dried as above. If the material under examination contains any hydrocarbons at all volatile at this temperature, it will of course be necessary to resort to other means of drying.

Analysis of Sample.—After drying, from 2 to 15 grm. (depending on the richness in bitumen of the substance) are weighed into a 150 c.c. Erlenmeyer flask, the tare of which had been previously ascertained, and treated with 100 c.c. of carbon disulphide. The flask is then loosely corked and shaken from time to time until practically all large particles of the material have been broken up, when it is set aside and not disturbed for 48 hours. The solution is then decanted off into a similar flask, that has been previously weighed, as much of the solvent being poured off as possible without disturbing the residue. The first flask is again treated with fresh carbon disulphide and shaken as before, when it is put away with the second flask and not disturbed for 48 hours.

At the end of this time the contents of the 2 flasks are carefully decanted off upon a weighed Gooch crucible fitted with an asbestos filter, the contents of the second flask being passed through the filter first. The asbestos filter shall be made of ignited long-fibre amphibole, packed in the bottom of a Gooch crucible to the depth of not over 1/8 inch. After passing the contents of both flasks through the filter, the two residues are shaken with more fresh carbon disulphide and set aside for 24 hours without disturbing, or until it is seen that a good subsidence has taken place, when the solvent is again decanted upon the filter. This washing is continued until the filtrate or washings are practically colourless.

The crucible and both flasks are then dried at 125° and weighed. The filtrate containing the bitumen is evaporated, the bituminous residue burnt, and the weight of the ash thus obtained added to that of the residue in the 2 flasks and the crucible. The sum of these weights deducted from the weight of the substance taken gives the weight of bitumen extracted.

In the analysis of hard asphalts or tar pitch for their solubility in carbon disulphide and also in the analysis of any of the bitumens for their solubility in naphtha, it is recommended that from 15 to 20 grm. of glass beads be introduced into the first flask with the substance. When the flask is shaken, these beads grind upon any hard lump of bitumen, and thus greatly facilitate the solution of the soluble constituents. In filtering these solutions through the Gooch crucible, they should be allowed to run through by gravity, as the application of an exhaust appears to cause a clogging of the filtering medium.

This test shall be carried on at a temperature of from 20° to 25°. When carbon disulphide or carbon tetrachloride are used as solvents, they must be chemically pure. When naphtha is employed, the committee recommends that in all cases it be described by stating its sp. gr. and the temperatures between which it distils.

For rapid work the committee suggests the following method as a convenient one to be employed. It is based in general upon the standard method, and is applicable to practically all bituminous compounds.

From 1 to 10 grm. of water-free material (depending upon the amount of bitumen present) are weighed into a 150 c.c. Erlenmeyer flask, the tar of which has been previously ascertained, and treated with 100 c.c. of carbon disulphide. The flask is then loosely corked and shaken from time to time until practically all large particles of the material have been broken up, when it is set aside for not less than 15 hours. At the end of this time the contents of the flask are decanted off upon a weighed Gooch crucible fitted with a long-fibre amphibole asbestos filter. The residue remaining in the flask is then washed with 50 c.c. of carbon disulphide, allowed to settle, and decanted as before, the insoluble matter being finally brought upon the filter and washed with 100 c.c. carbon disulphide or until the washings are practically colourless. The filter and contents are then dried at 125°, cooled and weighed. Should any residue remain in the flask, it is also dried and weighed and this weight added to that of the residue in the crucible. The filtrate should be burned off and ignited to an ash

and the weight of the ash thus obtained added to that of the insoluble residue. The weight of the total residue deducted from that of the original material gives the weight of the bitumen soluble in cold carbon disulphide. In case of tars and pitches the percentages of insoluble residue, determined as above, minus that of any ash which may be found by igniting a separate sample, is reported as free carbon. Glass beads may be employed in the flask, as described in the standard method by the determination of bitumen. This test shall be carried on at a temperature of from 20 to 25°.

Penetration.—The consistency, or penetration, of a bitumen shall be the distance, expressed in hundredths of a centimeter, that a No. 2 needle will penetrate into it at 25° (77° F.), in 5 seconds of time, under a weight of 100 grm., the needle to penetrate direct without friction.

Loss on Heating.—The loss of heating of oil and asphaltic compounds shall be ascertained in the following manner: 50 grm. of the water-free material shall be placed in a circular tin box with vertical sides, measuring about 1 in. in depth by 2 3/8 in. in diameter, internal measurement. The penetration of the material to be examined shall, if possible, be determined at 25° in the manner heretofore described, and the exact weight of the sample ascertained. The sample in the tin box shall then be placed in a hot-air oven, heated to 170°, and kept at this temperature for 5 hours. At no time shall the temperature of this oven vary more than 2° from 170°. When the sample is cooled to normal temperature, it shall be weighed and the percentage of loss by volatilisation reported. The penetration of the residue shall then, if possible, be determined at 25°, in the manner heretofore described, and the loss in penetration determined by subtracting this penetration from the penetration before heating.

Standard Method of Estimation of Residual Coke in Bituminous Compounds.

This estimation shall be made according to the method described for coal in the *J. of the Amer. Chem. Soc.*, 1899, Vol. 21, page 1116. The method is as follows: Place 1 grm. of pure bitumen, free from water, in a platinum crucible weighing 20 to 30 grm. and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for 7 minutes. The crucible should be supported on a platinum triangle with the bottom 6 to 8 cm. above the top of the burner. The

flame should be fully 20 cm. high when burning free, and the determination should be made in a place free from draughts. The upper surface of the cover should burn clear, but the under surface should remain covered with carbon.

The residue minus the small impurity of ash in the pure bitumen is the fixed carbon, which should be calculated to 100% with the volatile hydrocarbons, excluding the inorganic matter.

Standard Method of Sizing and Separating Aggregate in Asphalt Paving Mixture.

The method consists of passing the mineral aggregate through several sieves of the following sizes:

	Inches in diameter
10-mesh per linear inch, size of wire	0.027
20-mesh per linear inch, size of wire	0.0165
30-mesh per linear inch, size of wire	0.01375
40-mesh per linear inch, size of wire	0.01025
50-mesh per linear inch, size of wire	0.009
80-mesh per linear inch, size of wire	0.00575
100-mesh per linear inch, size of wire	0.0045
200-mesh per linear inch, size of wire	0.00235

The following methods, pages 73 to 84, are those proposed by Clifford Richardson.

Water, Ordinary Method.—Ordinarily it is sufficiently accurate to weigh out 2 to 5 grm. of the material in a crucible, preferably on a watch-glass, to expose more surface, and to subject it to a temperature of 100° in a well-regulated water-bath, until it ceases to lose in weight to an extent of more than 0.2 to 0.3% on successive heatings. A greater concordance is not sought, as many asphalts continue to lose light oils at this temperature. The degree of fineness to which the crude asphalt should be reduced before weighing out is dependent upon the amount of water it contains. In powdering some asphalts, such as crude Trinidad, the material, since it contains 29% of water in emulsion with bitumen, begins to lose water at once. It can, therefore, only be broken into coarse lumps and not reduced to a powder until after a preliminary determination of the water thus lost by the coarse material. Other asphalts, containing only a small amount of hygroscopic or adventitious water, may be ground up at once, while some which are not readily powdered may be cut into small pieces. (If

it is necessary to determine the water absolutely, it may be estimated
by a method of distillation as given by Marcusson, or by the " Reviser "
in the *Jour. Ind. and Eng. Chem.*, 1910, **2**, 66.)

Alternate Method.—For asphalts such as crude Trinidad, in which
the difficulties described are met, a different method of procedure
is advisable. The substance is very quickly reduced to a coarse powder
only in a mortar provided with a cover, through which the pestle
passes. 5 grm. of it are spread out on a 4-in. watch-glass, and
this is placed *in vacuo* over sulphuric acid for 12 hours and the
loss determined. It should then be reground to a fine powder and
exposed again *in vacuo* until it ceases to lose weight. The loss may
be stated as water.

In whichever way the asphalt is dried a sufficient quantity is pre-
pared and preserved in this condition in a tightly stoppered bottle,
for analysis. Asphalts which cannot be reduced to powder are used
in mass.

Refined Asphalts.—Examination of refined asphalts in their most
extended form include the determinations given on the accompanying
form, used as a convenience in reporting. With well-known asphalts
but a limited number of determinations are necessary for the purpose
of detecting lack of uniformity or peculiarities in the material.

Physical Properties.

Sp. gr., 25.5° /25.5°; original substance, dry ....
Sp. gr., 25.5°, pure bitumen ....
Colour of powder or streak................................
Lustre...
Structure...
Fracture..
Hardness, original substance............................
Odour...
Softness..
Flows ....
Penetration at 25.5°......................................

Chemical Characteristics.

Original substance:
    Loss, 100°, 1 hour................................
Dry substance:
    Loss, 162.7°.....................................
    Character of residue.............................
    Penetration of residue at 25.5°..................
    Loss, 204.4°, 7 hours (fresh sample).............
    Character of residue.............................
    Penetration of residue at 25.5° ....
    Bitumen soluble in CS_2, air temperature ....
    Organic matter insoluble ....
    Inorganic or mineral matter.....................

Malthenes:
    Bitumen soluble in 88° naphtha, air temperature......
    (This is given in % of total bitumen)...............
    % of soluble bitumen removed by H_2SO_4..........
    % of total bitumens as saturated hydrocarbons ......
    Bitumen soluble in 62° naphtha.....................
    (This in % of total bitumen).......................
Carbenes:
    Bitumen insoluble in carbon tetrachloride, air temper-
        ature..
    Bitumen soluble in carbon tetrachloride, air temperature
Bitumen yields on ignition:
    Fixed carbon....................................
    Sulphur...
    Ultimate composition...... ....
Remarks:

The comprehensive scheme for the analysis of asphalts and fluxes is taken from "The Asphalt Pavement," by Clifford Richardson, Wiley and Sons, New York, 1905. This is done for the reason that the methods are quite practical and briefly stated and probably represent recent practice better than any other scheme that has been published. The special methods of Sadtler and Linton, referred to below, are given in addition, however, as they are of experimental value and are referred to frequently in the literature on asphalts.

Physical Properties.—Sp. gr.—The sp. gr. of the dried asphalt is taken in a pycnometer at 25°, and referred to water at the same temperature.

The usual determinations of the outward physical features of any mineral substance, colour of streak, structure, fracture, hardness, and odour, if any, are noted.

The colour of the streak or of the powder of a hard asphalt is in certain cases characteristic. For example, in the case of refined Trinidad lake asphalt the powder is a bluish-black colour, while that of the refined Trinidad land asphalt is much browner. Powdered gilsonite is of a very light-brown colour. Powdered grahamite is quite black.

The structure of a solid native bitumen may be either homogeneous or it may show the presence of cavities containing gas, particles of adventitious mineral matter, shale or clay, or other peculiarities.

The fracture may be, in the case of very pure bitumens, conchoidal or semi-conchoidal, pencillated, or hackley in the case of grahamite, or irregular.

The hardness of the original material, if it contains much mineral matter, may be stated in degrees of Mohr's scale, that of the pure

bitumen in several ways. It is either brittle, like glance pitch, or soft enough to be penetrated with the needle of a penetration machine, in which case the hardness is expressed in degrees of this machine.

The odour in the case of many bitumens is characteristic. That from Venezuelan asphalt, found near the Gulf of Maracaibo, is extremely strong and rank, while others are more purely asphaltic, especially on warming. The heat in any case brings out the odour to a degree not observed in the cold material.

Loss on Heating.—It is sometimes necessary to determine the loss which an asphalt suffers on heating for a time to a definite temperature. The length of time has been arbitrarily taken as seven hours and the temperature 162.7° and 204.4°.

The determination is made as follows: In a No. 1 crystallising dish, 2 1/4 in. in diameter and 1 5/16 in. high, are placed 20 grm. of the material under examination.

Should it be necessary to use a very much larger dish the weight of the material to be taken should be calculated so that the volume which it holds shall bear the same relation to the surface exposed as in the case with the smaller dish. It is necessary to take separate portions of the substance for each determination, and not to attempt to determine the loss at 204.4° from the sample which has been previously heated at 162.7°.

The dish is heated to the requisite temperature for the given length of time in an oven, the temperature of which is uniform in all parts. This is something that is not as easily accomplished as might be supposed. The thermometer in an ordinary oven does not indicate the temperature in all its parts; in fact, only where the bulb of the thermometer itself is placed. Such an oven is not only difficult to obtain, but the manner in which the best form is used is of great importance.

Softening and Flowing Points.—The solid native bitumens can have no definite m. p. for the reason that they are composed of mixtures of hydrocarbons. It is only possible, therefore, to determine rather arbitrarily the points at which the material softens and flows and with special reference to the relation of these points toward some standard bitumen. They are determined as follows:

A crystallising dish, of the same form as that used for determining the loss on heating at 162.7° and 204.4°, is placed upon a ring-stand over an asbestos plate or wire gauze where it can be heated by a

small flame. It is than filled with clean metallic mercury to a distance of 1/4 in. from the top. On the surface is placed a thin microscope cover-glass, No. oo, carrying the specimen of asphalt under examination and a second glass containing a sample of known softening point as a standard of comparison. The complete apparatus consists of a crystallising dish as above described, a funnel with its stem cut off close to the angle to serve as a cover, a few microscopic cover-glasses, and a thermometer.

The specimens are prepared for the experiment in the following manner: When dealing with hard asphalts that can be ground rather coarsely, minute fragments are spread on the cover-glass and placed upon the surface of mercury, covered with a funnel, and a thermometer passed through the orifice of the funnel until the bulb is immersed in the mercury. It is held in position by a clamp attached to the ring-stand holding the dish. A burner that can be regulated to a small flame is placed under the dish and it is heated so that the rise of temperature will not be more than 2 to 3° F. per minute. In a short time it will be noticed that the specimens will have changed from the brown or the yellowish-black colour of the powder to that more nearly approaching the original, with a slight rounding of the individual grains. This is taken as the softening point. On further heating, these globules flow together and from a thin sheet on the glass. The point at which the specimens begin to soften and the beginning of the flow, as indicated by the thermometer, are noted as the softening and flowing points.

Asphalts that cannot be ground are treated as follows: The material is softened and pulled out to a thread 1 mm. in diameter and several small pieces 1 mm. in length cut from it. These should be placed on the glass together, as one will serve as a check on the other and thereby lessen the chance of error. The softening point may be noted by the rounding of the particles and the beginning of the flow, or when the specimen begins to spread out, which is always at the point of contact with the cover-glass, is set down as the flowing point or the temperature at which the specimens will flow perceptibly.

Estimation of Total Bitumen.—1 grm. of the dried or refined material in a state of very fine powder, if possible, is weighed out and introduced into a 200 c.c. Erlenmeyer flask of Jena glass and covered with about 100 c.c. of carbon disulphide. It is then set aside for at least five hours or overnight, at the temperature of the laboratory.

In the meantime a Gooch crucible is prepared with an asbestos felt and weighed. This Gooch crucible is of special form with a large filtering surface. It holds 30 c.c., 4.4 cm. at the top, tapering to 3.6 cm. at the bottom and 2.6 cm. deep. This is much better for percolation work than the usual narrow form of Gooch. It is furnished by Eimer and Amend, New York. The felt is made by beating up long-fibre Italian asbestos in a mortar, and suspending the finer particles in water and quickly pouring off from the coarse particles. Too much of the latter should not be removed, or the felt will be too dense. The decanted asbestos and water can be kept in a bottle for use. To prepare the felt the asbestos and water are shaken up and what is found to be a proper amount poured into the crucible, which has in the meantime been attached to a vacuum filtering-flask by the proper glass and rubber connections. As soon as the asbestos has somewhat settled the vacuum-pump is started and the felt firmly drawn on the bottom of the crucible. It is then dried, ignited, and weighed.

After standing a proper time, the bisulphide is decanted very carefully upon the filter which is supported in the neck of a wide-mouthed flask and allowed to run through without pressure. The flask after being tipped to pour the first portion is not again placed erect in order to avoid stirring up the insoluble material, but is held at an angle on any suitable base, such as a clay chimney. After all the bisulphide is decanted more is added and the insoluble matter shaken up with it. This is allowed to settle and decanted as before, the insoluble matter being finally brought on the filter and washed with the solvent until clean. The excess of bisulphide is allowed to evaporate from the Gooch crucible at the temperature of the room. It is then dried for a short time at 100° and weighed. The loss of weight is the percentage of bitumen soluble in CS_2.

In the meantime, however, the bisulphide which has passed the filter is allowed to subside for 24 hours, if possible, and is then decanted carefully from the flask from which it has been received into a weighed platinum or unweighed porcelain dish. If there is any sediment in the flask it must be rinsed back into the Gooch crucible with bisulphide and the crucible again washed clean. The solvent in the dish is placed in a good draught and lighted. When all the bisulphide has burned, the bitumen remaining in the dish is burned off over a lamp and the mineral residue, which was too fine to subside, is weighed, if

the burning was done in a platinum dish, or dusted out and added to the crucible if in a porcelain one. In the former case the weight is added to that of the Gooch crucble or subtracted from the % of the bitumen, found without its consideration, as a correction. Care must be used in this method of procedure that the solvent does not creep over the sides of the crucible and that the outside is free from bitumen before weighing. In order to avoid this the crucible is supported in the neck of a flask with three constrictions, the neck extended above the top of the crucible and the latter being covered with a watch-glass. (These flasks are made for Mr. Richardson by E. Machlett & Son, 143 East 23d Street, New York.)

Mineral Matter or Ash.—1 grm. of the same sample of material used for the estimation of bitumen is weighed out in a No. o Royal Berlin porcelain crucible and burned in a muffle or over a flame until free from carbon. This must be determined by breaking up the cake of ash, moistening with water or alcohol, and observing if any black particles of coke are present. The weight of the residue is stated as inorganic or mineral matter.

The estimation is of course not exact, sulphuric acid and the alkalies being volatilised in many cases, but it is satisfactory for technical purposes.

Organic Matter Insoluble.—The amount of this material, sometimes stated as organic matter not bitumen, is obtained by difference; that is to say, by subtracting the sum of percentages of bitumen and inorganic matter found from 100. It, of course, includes all the errors in these 2 estimations, and as the error in the bitumen is one making the percentage too high, and in that of the mineral matter too low, the errors are cumulative, do not neutralise each other, and the percentage of organic matter not bitumen is thus always too high.

If hot carbon bisulphide, chloroform or spirits of turpentine are used as solvents for the bitumen, the amount obtained on extraction is somewhat greater, but in technical work the results are no more desirable and such solvents are not often used, as chloroform is expensive where a large number of estimations are carried out and the spirits of turpentine are so much more viscous that they filter much less readily, while the residue of this solvent remaining on the filter must be removed by naphtha and not by evaporation.

The sum of the 3 estimations, bitumen soluble in CS_2, organic not soluble, and inorganic matter, is, therefore, always 100%.

Naphtha Soluble Bitumen.—For the purpose of determining the percentage of bitumen soluble in naphtha, distillates of 88° and 62° B. are used. It is extremely important that these naphthas should be of the exact degrees specified, since differences in density will make appreciable differences in the amount of bitumen extracted. The distillate should be that obtained from a petroleum with so-called paraffin base. The density of each lot should be carefully determined with a Westphal balance at 15.5°, and if it is too dense it should be rejected. On the other hand, if it is too light it can be brought to the proper density by blowing a current of air through it for a short time, at the ordinary temperature in the case of the 88° and, after slightly warming it, in the case of 62° naphtha. Redistillation of these naphthas is unnecessary as the products of the distillations are no more uniform than the original naphthas.

It will be found very necessary that hard bitumens should be reduced to an impalpable powder before attempting to extract them, as otherwise the extractions will not be complete. The softer bitumens should be divided as much as possible.

The bitumen is usually extracted with naphtha of both densities in order to determine the differences in their action. If the amounts extracted by each is the same or nearly the same it will point to the fact that the bitumen consists of hard asphaltenes mixed with light malthenes, the latter equally soluble in naphtha of both degrees of sp. gr., and but little of intermediate hydrocarbons, or of the very hard asphalt fluxed artificially with some light oil. If, on the other hand, there is a very considerable increase in the percentage dissolved by the 62° over the 88° naphtha it may be assumed that the malthenes are well-graded and natural constituents of the bitumen which is being examined. In certain cases, however, the use of the two naphthas is unnecessary. It would be useless to extract a maltha with a dense naphtha or glance pitch or albertite with a lighter one.

It appears, therefore, that heating increases the density of naphthas, and consequently their solvent powers, from inability to condense the more volatile parts, but that the change in the 62° naphtha is small, so that it can safely be heated to a slight extent.

As a result of these experiments all determinations are now made with cold naphtha by the following method:

1 grm. of the substance is weighed into a 200 c.c. Erlenmeyer flask, covered with naphtha and allowed to stand, as in estimating total

bitumen; in fact, the entire process is the same with the exception that one or two precautions must be observed. It is well not to attempt to break up any lumps with a stirring rod, as the substance, especially the softer asphalts, may then adhere to the rod or flask and be difficult to detach.

It may also be necessary to treat the substance with several portions of the solvent instead of with 2 or 3, as in the case of carbon bisulphide. No heat is applied at any time on the process.

Fixed Carbon.—The fixed carbon is determined usually on the pure bitumen according to the method recommended by the Committee on Coal Analysis of the Amer. Chem.

FIXED CARBON IN BITUMENS.

	Extremes		High grade
	High	Low	
Grahamite...	53.3	35.3	53.3
Albertite...	54.2	29.8	29.8
Gilsonite...	26.2	3.3	14.5
Manjak, Barbadoes.................................	....	....	15.0
Asphaltenes from Trinidad bitumen.................	....	....	25.8
Glance pitch......................................	30.0	15.0	15.0[1]
Asphalt...	17.9	10.8	14.2
Byerlyte (artificial asphalt).....................	....	....	14.3
Standard Asphalt Co's. mine, soft gilsonite.......	....	....	17.3
Malthenes from Trinidad bitumen...................	....	....	6.3
Wurtzilite, Utah..................................	6.8	5.3	8.2
Residuum, Pennsylvania field......................	....	....	3.4
Sunset oil, Kern Co., Cal.........................	....	....	2.7

The residue minus the small impurity of ash in the pure bitumen is the fixed carbon, which should be calculated to 100% with the volatile hydrocarbons, excluding the inorganic matter. As the committee states, this determination, like most industrial ones, is arbitrary, but it is of the greatest value in determining the nature of a bitumen quickly. Experience has shown that true hard asphalts have never been found which yield more than 17.9% nor less than 10.0% of fixed carbon, while grahamite yields over 53%, albertite over 29 to 54%,

[1] Egyptian.

and some other bituminous materials characteristic amounts of fixed carbon.

Estimation of the Amount of Hard Paraffin Scale.—The amount of hard paraffin scale contained in any flux or heavy oil can be readily determined by Richardson's modification[1] of the method of Holde.[2]

The method in detail is as follows:

The Estimation of Paraffin in Petroleum Residues, Asphaltic Oils, and Asphalts fluxed with Paraffin Oils.—For this purpose, 1, 2, or more grm. of the substance to be examined is taken and covered with 100 c.c. of 88° naphtha in an Erlenmeyer flask. The amount will depend on the amount of paraffin present and on the percentage of oil which remains after the preliminary treatment with naphtha and acid. Of a residuum from eastern pipe-line oils 1 grm. is sufficient, as the substance consists of a nearly pure bitumen containing from 4 to 12% of paraffin. 10 grm. of a residual pitch from Beaumont oil should be used, as this, in some cases, contains only 65.0% of its bitumen soluble in naphtha, less than 50% unacted on by acids, and only about 1.0% paraffin. Several grm. can be taken of a Trinidad asphalt cement, made of asphaltum and Pennsylvania residuum, which contains 26.0% of mineral matter and only 70.0% of its bitumen is in a form soluble in 88° naphtha.

The object of the naphtha treatment is to separate the paraffin from substances of a non-bituminous nature and from some of the asphaltic hydrocarbons insoluble in naphtha which would be precipitated in the ether alcohol solvent and contaminate the paraffin.

The naphtha is allowed to act on the substance overnight, and the next morning the solution is decanted through a Gooch crucible. The residue is washed well with naphtha and the combined solution and washings united. If desired, the residue, insoluble in naphtha, remaining on the asbestos felt, can be weighed and the amount of soluble bitumen determined by difference. In the case of carefully prepared residues from paraffin petroleum, this naphtha solution may be evaporated in the flask in which the paraffin is to be separated and the subsequent determination by the Holde method carried on with this residuum or bitumen soluble in naphtha, but, as will be seen, the results

[1] *J. Soc. Chem. Ind.*, 1902, **21**, 690.
[2] Mitt. a. d. könig. tech. Vers.-anst., Berlin, 1896, **14**, 211. Abs. *J. Soc. Chem. Ind.*, 1897, **16**, 362; Lunge, Chem. Tech.; Untersuchungs Methoden 3, 9.

obtained are too high. Where asphaltic oils are present in the naphtha solution bitumen, and preferably in all cases except those of distillates, a further treatment is necessary to remove oils, which would otherwise be thrown out, from the ether solution with the paraffin by the alcohol. For this purpose the naphtha solution is placed in a separating funnel and shaken with sulphuric acid, sp. gr. 1.84, until a fresh portion of acid is but slightly coloured. Twice is generally sufficient. The solution is washed with water several times, then with a weak solution of carbonate of soda, again with water, and the bitumen in solution recovered, weighed, if desired, and treated by the Holde method for the separation of the paraffin it contains. By this means all the unsaturated hydrocarbons and those of an asphaltic nature, readily precipitated by alcohol from their ether solution, are removed and the possibilities brought about of recovering the paraffin in a pure condition.

Some determinations made in the manner described resulted as follows:

PETROLEUM RESIDUUM FROM PIPE-LINE OIL.
Sp. Gr., 0.93.

No.	Weight taken, grm.	Soluble in naptha, %	Not acted on by H_2SO_4, %	Paraffin, %
1	1.0	96.0	No treatment	7.95
2	1.0	96.0	89.5	5.55
3	1.0	Distilled *in vacuo*	No treatment	5.95

TRINIDAD ASPHALT CEMENT.

No.	Weight taken, grm.	Soluble in naphtha	Not acted on by H_2SO_4	Paraffin
1	10.0	....	No treatment	2.95
2	10.0	....	Treated	0.95

In each case the paraffin recovered after treatment was white and pure, while that obtained in the other way, even by distillation *in vacuo*, was coloured. The results after treatment were, of course, lower and more correct.

The Trinidad asphalt cement was made from 100 parts of Trinidad asphalt and 20 parts of a residuum similar to the one analysed. The

asphalt contained, of course, no paraffin; the residuum, 5.55%. The calculated amount in the cement is therefore 0.925%, and 0.95% was found.

In this way it can be determined whether the flux which has been used in the preparation of an asphalt cement has been derived from a paraffin petroleum or from one having an asphaltic base, since, if paraffin is found to such an extent as shown above, it will necessarily point to the use of a paraffin flux, as no native solid bitumen in use in the paving industry contains paraffin.

Non-bituminous Organic Matter and Ash.—As noted above, the organic matter not soluble in the various solvents used for fractionating the asphalt is noted as "non-bituminous organic matter" or by some similar descriptive term. It is estimated by difference; the total residue left after the various solvents have exhausted their action is dried, ignited until all carbon has disappeared, and weighed again. The loss of weight has been by most authorities considered to be non-bituminous matter. It has been found by Richardson, however (*Proc. Am. Soc. Test. Mat.* (1906), **6**, 509), that clays absorb certain amounts of bituminous matter, so that what has generally been considered organic non-bituminous matter[1] is probably bituminous and should be largely included with the amount of bitumen found. It is obvious that if the original matter contained notable amounts of carbonates, the total loss will include the carbon dioxide that has escaped. To correct this, the ash may be recarbonated by allowing it to remain some hours in contact with a solution of carbon dioxide in water, or by heating it with ammonium carbonate solution, evaporating, and heating gently. Ash may, of course, be determined directly, without extraction. This will give a more accurate result in some cases, in consequence of the solubility of some of the mineral material in the solvents used. The detailed examination of the ash is conducted according to the usual methods for clay, limestone, or sand stone, as the case may be.

Sulphur.—Richardson recommends Mabery's method—combustion in a current of oxygen and absorption of the sulphur dioxide by standard alkali. Day (*J. Frank. Inst.*, **140** (1895), 221) found considerable difficulty in determining sulphur in a specimen of Utah

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[1] F. C. Garrett in a private communication to the reviser of this section seems to differ in opinion from Clifford Richardson who considered the organic non-bitumen that had previously been reported as non-existent and due to the adsorptive effect of the mineral matter. Garrett examined it microscopically and found it to consist largely of vegetable matter (cellulose, etc.).

gilsonite, owing to the liability of sulphur compounds to distil before oxidation. He finally succeeded by oxidising the material in an open vessel with strong nitric acid by aid of heat. In time the material dissolves completely to a dark red liquid. When this condition is reached, the solution should be poured into cold water, by which a reddish-brown precipitate is formed, which contains all but traces of the sulphur. This mass is well-washed, and the sulphur determined by Eschka's method.

E. H. Hodgson (*J. Amer. Chem. Soc.*, 1898, **20,** 882) has made tests of several methods for estimating sulphur in asphalts, and finds that Carius' method—oxidation by fuming nitric acid—gives the best results, but is tedious and liable to explosion. This process is thus described: The tubes used were made of heavy glass. Three determinations are started on each sample, one with from 1 to 2 grm. of oil, depending upon the amount of sulphur expected, the others with less. The sample, in a small bulb blown from small-bore tubing, is placed at the bottom of the Carius' tube. To fill, the bulb is heated to expand the air in it and allowed to cool with the end which is drawn down to a capillary held under the oil, both while heating and as it cools. After the sample bulb is at the bottom of the tube, 15 c.c. of fuming nitric acid (sp. gr. 1.60) poured on. The open end is then drawn out fine, but not sealed, endeavouring while doing so to thicken the walls by allowing them to be drawn together, rather than become thin by being pulled out too quickly. The tube is then heated for about 6 hours in water kept at from 80° to 90°, 5 c.c. more of acid are added, the tube is sealed, and heated in a guarded oven (on account of danger of explosion) at 150° for from 4 to 5 hours. Allow the tube to cool, open, reseal, and heat again for from 2 to 4 hours at a temperature of 180° to 200°. Cool, open, and remove the liquid to a beaker of 250 c.c. capacity; dilute with water, filter, and wash. If the residue contains anything but sand, it is saved and treated separately. The filtrate is evaporated to dryness on the water-bath, adding a piece of sodium hydroxide. The nitrates are completely decomposed by repeatedly evaporating the solution with hydrochloric acid and the silica rendered insoluble by heating to 110° in an air-bath. The mass is cooled, 2 or 3 c.c. of hydrochloric acid added, then 100 c.c. of water, the mixture stirred, filtered, the filter well washed, and the filtrate diluted to 200 c.c., heated to boiling, and 20 c.c. of a 20% solution of barium chloride added from a burette at the rate of about 1 drop

each second, stirring all the time.   After the barium chloride has been added, boil for about 10 minutes and then allow to stand 24 hours. Filter, wash with hot water, dry, ignite, cool, moisten with sulphuric acid, re-ignite, cool, and weigh.

The double crucible method of S. S. Sadtler described on page 52 is perfectly applicable for asphaltic materials of all kinds, and in fact it is more suited for this class of materials than for crude oils, for with very volatile compounds precautions are necessary to prevent too rapid volatilisation of the oil.

The methods employing sodium dioxide or nitrates are apt to be too low.

Older Methods of Fractionation of Asphalts.—The results obtained by the following processes are more or less arbitrary, and cannot be regarded as true proximate analyses; but it must be borne in mind that engineers have reached certain opinions as to qualities of asphalts for special purposes, and have interpreted the analytic data in accordance with these practical results; hence in examining newly-discovered asphalts it may be necessary to use the older methods, even if improved processes should also be employed.

Bermudez asphalt requires a somewhat different method, owing to its sticky nature which prevents its drying, by being powdered and exposed to the air.   The samples may be heated to the softening point, but some volatile matter other than water will be lost.

Linton's Method of Fractional Separation of Constituents. (*J. Amer. Chem. Soc.*, 1894, 820; 1896, 276).—The dried sample is weighed on a tared filter, which is then placed in a separatory funnel, 50 c.c. of petroleum spirit poured on, allowed to remain a few minutes, and then drawn off, more of the spirit is then added and also soon drawn off.   It is necessary that the first portions of solvent should not become highly charged with soluble matters, since these may be precipitated as the liquid runs out of the funnel.   When the mass is nearly exhausted, the later portions of solvent may be left for some hours in contact with the sample.   The extraction must be carried on until the solvent ceases to be coloured.   The filter and its contents are dried in a steam-bath and weighed; the loss of weight represents that portion of the asphalt commonly designated as petrolene.

The filter and contents are placed in the separator-funnel, enough boiling oil of turpentine added to cover them, and the mixture allowed to stand for some hours or overnight.   The process must be repeated

with fresh portions of boiling oil of turpentine until the filtrate is colour-less. The mass is now treated with chloroform sufficient to cover it, and at least an hour allowed for solution. Washing with chloroform is continued until it passes through colourless. The residue is dried and weighed; the loss is designated asphaltene. The filter and contents are burned in a platinum crucible, and if the sample originally con-tained a notable amount of calcium carbonate the residue should be re-carbonated before weighing.

Sadtler's Method (*J. Frank. Inst.*, **140** (1895), 385).—An asbestos filter is made in a weighed Gooch crucible and dried. About 10 grm. of fine white sand, previously ignited and cooled, are added, a piece of stout platinum wire 7 or 8 cm. long is placed in the crucible, and the whole dried to constant weight at 100°. One to 2 grm. of the sample in fine powder are added, gently mixed with the upper portion of the sand layer with the aid of the platinum wire, care being taken not to disturb the asbestos filter. If the sample be a liquid bitumen, it is gently mixed with the sand layer after slightly softening with aid of the drying oven. The weight of the whole is accurately taken, and then dried at 100° to a constant weight in an air-bath or water-oven, cooled in a desiccator, and weighed. The crucible and contents are placed in a continuous extraction apparatus formed by placing a small conical percolator within a larger one, the inner one being held in position by a perforated cork. The crucible is placed in the inner percolator; the outer one is connected with a flask containing pure acetone, and with an upright condenser. The flask is heated by a water- or sand-bath. Acetone is first used and the operation continued until the loss on continuing the extraction for 2 hours does not exceed 2 mgm. The loss of weight computed on the weight after drying is designated petrolene. The extraction is then continued with chloro-form, and the additional loss is designated asphaltene. The duration of the total extraction varies with different samples, but usually twelve hours for the acetone and eight hours for the chloroform will suffice. The loss of weight should be taken every four hours at first, and then every 2 hours until the extraction is complete, the crucible and contents being dried at 100° each time and cooled in a desiccator. The final residue in the crucible is considered to represent the non-bituminous organic and mineral matter. It is ignited after placing the cap on the bottom of the crucible and weighed; the loss is designated non-bituminous matter; the residue, mineral matter or ash.

F. C. Garrett (private communication to the reviser of this section) states that a volatility factor may be obtained by dividing the volatile matter by the fixed carbon when a proximate analysis is made. He also states that volatility factor of Trinidad lake pitch is above 5, of land pitch between 4 and 5, of an asphaltite (Maryak) a little above 3.

The following analyses were communicated by F. C. Garrett:

Sample I. Manjak from Vista Bella Mine, Sunidad (dull).
Sample II. Manjak from another specimen (coal bright).
Sample III. Hard pitch from Parker Mine. Cacarajicara, Cuba.
Sample IV. Elastic Elaterite from Derbyshire.

	I	II	III	IV
Moisture	0.46	0.80	....	....
Volatile matter	57.28	59.05	53.55	96.71
Fixed carbon	37.36	36.25	45.00	1.09 (soot)
Ash	4.89	3.90	1.45	2.20
Total	99.99	100.00	100.00	100.00
Sulphur	2.96	3.05	8.47	1.14%

Comparison of Methods.—It is obvious that these methods will not give strictly comparable results on even the same specimens, and that the designation of particular fractions as petrolene or asphaltene without indicating the method of extraction, may be misleading. Their value lies largely as a means of identification or for purposes of comparison.

The following analysis from Richardson shows that a large part of the sulphur is in the portion insoluble in naphtha:

Carbon.. 82.01%
Hydrogen... 7.82%
Sulphur.. 10.86%
Nitrogen...   ?

                                            100.69%
Sp. gr. (acid free)................................ 1.121

The naphtha-soluble bitumen has the following composition:

Carbon.. 84.59%
Hydrogen... 11.30%
Sulphur.. 2.91%
Nitrogen... 0.59%

                                             99.39%

Naphtha-soluble Bitumen Purified with H_2SO_4.

Sp. gr.	0.9758
Carbon	86.44%
Hydrogen	12.66%
Sulphur	0.45%
Nitrogen	0.07%
	99.62%

Peckham (*J. Frank. Inst.*, 1896) has compared the results of the application of Linton's and Sadtler's methods to identical samples, and finds considerable differences. He gives the following figures. The exact nature of the sample marked "épurée" is not stated, but it is not the ordinary refined asphalt.

Linton's Method:

	Trinidad asphalt.	
	Crude.	Epurée.
Soluble in petroleum spirit	33.73	33.62
Soluble in boiling oil of turpentine	10.51	15.57
Soluble in chloroform	8.12	2.67
Total bituminous matter	52.36	51.86
Organic matter not bitumen	10.85	10.15
Mineral matter	36.72	37.97

Sadtler's Method:

Soluble in acetone	28.18	26.31
Soluble in chloroform	27.00	29.17
Total bituminous matter	55.18	55.48
Organic matter not bitumen	9.83	9.60
Mineral matter	34.98	34.92

A sample of very dry Egyptian asphalt and one from the Athasbasca River region were selected as representing the extremes of variation in composition, and the solubilities in petroleum spirit and acetone compared, as follows:

	Egyptian	Athasbasca
% soluble in acetone	8.68	24.33
% soluble in petroleum spirit	38.03	73.86

Acetone should not be substituted for petroleum spirit unless notice is given in the report of analysis.

Sadtler furnishes the following figures obtained by the acetone method, but gives no comparative analyses. It is to be noted that the Trinidad and Bermudez samples were the commercially refined.

	Trinidad	Bermudez	Alcatraz (liquid)
Soluble in acetone..........	46.40	66.47	89.21
Soluble in chloroform......	15.14	29.66	9.39
Organic matter not bitumen......	3.02	1.76	trace
Mineral matter..............	35.44	2.11	1.40

In the report of the Commissioners of Accounts of New York City, Prof. Peckham refers to the fact that Dr. S. P. Sadtler had suggested a systematic examination of different natural bitumens with different solvents of fixed purity, and presents a brief account of work he was engaged in of this nature in treating Trinidad pitch. He first used 95% methyl alcohol, then pure acetone, next ethyl ether, and finally pure chloroform. In each case a certain amount passes into solution, the larger amount going into solution with the acetone and chloroform. In all cases, however, the material extracted seemed to be distinctive and not as Dr. Endemann suggested that no clear lines of demarcation would be found.

ULTIMATE COMPOSITION OF ASPHALTS.

The ultimate composition of an asphalt will, as a rule, be of little value in determining its application in engineering or industrial operations. The amount of sulphur and nitrogen may be of some moment. The former is regarded by Richardson as influencing materially the hardness of the asphalt by inducing polymerisation, but this view has not been accepted by all experts in this field. The oxidation of the sulphur, which is probably mostly present in combination with hydrocarbons, in forms analogous to the mercaptans, may produce acids which will injure the asphalt proper or the paving mixtures made with it. Nitrogen is usually present in small amount, and, in part at least, in the form of pyridine derivatives.

The following explanation of the absence of oxygen is quoted from Richardson (*J. Soc. Chem. Ind.*, **17**, 29, 1898).

"According to Dana's Mineralogy, 'asphaltum or mineral pitch is a mixture of different hydrocarbons, part of which are oxygenated;' and it is stated that 'the fluid kinds change into the solid by the loss of a vaporisable portion on exposure, and also by a process of oxidation, which consists first in a loss of hydrogen, and finally in the oxidation of a portion of the mass.' Many other writers on the subject also express the same views. For the purpose of determining how far these statements were to be relied upon, since my earlier investigations of the bitumens of Trinidad, Bermudez, and some other asphalts had not shown that they contain oxygen, I have had complete ultimate analyses made of most of the pure bitumens previously examined for sulphur, and the results have been given in the same table. It is evident that among this large number of malthas and asphalts there are none, the soluble bitumen of which contains oxygen to an appreciable extent, although they all contain sulphur and nitrogen. It is, however, easy to explain how the earlier analyst reported oxygen as a constituent of many asphalts. As shown by several recent investigators, the complete combustion and estimation of carbon and hydrogen in the higher hydrocarbons is an extremely difficult thing, the tendency being toward the formation of acetylene and unsaturated hydrocarbons instead of carbonic acid and water, so that there is a deficiency in the amount of the latter found in an analysis, unless the greatest care is used. This had been commonly and naturally stated as oxygen. At the same time most analyses ignored the presence of sulphur and nitrogen, so that the amount of these elements is included in the stated percentage of oxygen. It is not surprising, therefore, that oxygenated hydrocarbons are frequently spoken of as occurring in asphalt, and it is equally plain that none exist in the bitumens of which they are composed. With the amount of sulphur present in most of them this is not surprising, as this element easily substitutes oxygen in most of the hydrocarbon derivatives."

The following figures are taken from results given by Richardson (*Ibid.*, **17**, 29 (1898), who gives all the elements present in the bituminous matter. In each case the percentage is calculated upon the extracted bitumen.

The figures for the sulphur are instructive when compared with the consistency. As a rule, it is highest in hard asphalts and lowest in malthas.

ULTIMATE COMPOSITION OF THE BITUMEN OF ASPHALT, MALTHAS, ETC. (HARD ASPHALT).

	Consistency	In extracted bitumen				
		S	C	H	N	Total
Nevada........................	Pitch.......	9.76	79.58	9.31	1.30	99.95
Texas, Uvalde Company.........	Hard.......	9.60	80.32	10.09	0.28	100.20
Italy, Ancona.................	Pitch.......	9.39	79.56	8.80	1.40	99.15
Egypt.........................	Pitch.......	8.52	80.87	10.42	0.19	100.00
Cuba, Bejucal.................	Pitch.....	8.28	82.98	9.44	0.09	100.79
California, Waldorf............	Hard.......	6.48	82.77	10.62	0.35	100.21
California, LaPatera..........	Hard.......	6.23	83.30	9.88	0.70	100.11
Trinidad lake.................	Hard.......	6.16	82.33	10.69	0.81	99.99
Tobago........................	Pitch.......	6.16	83.37	10.54	0.50	100.57
Turkey........................	Hard.......	6.14	83.98	9.19	0.09	99.40
Montana, hardened.............	Hard.......	5.31	.....	.....	....	......
California, Santa Maria........	Cheesey....	5.69	82.79	11.58	0.48	100.54
Trinidad, land................	Hard.......	4.98	83.65	10.76	0.45	99.94
France, South.................	Hard.......	4.78	82.07	11.58	1.56	99.99
Venezuela, Bermudez, hard......	Medium....	3.93	.....	.....	....	......
Sicily, rock..................	Medium....	3.69	84.95	11.34	0.33	100.31
Kentucky......................	Medium....	3.39	84.16	11.52	1.58	99.65
Texas, Rio Grande.............	Medium....	3.28	.....	.....	....	......
Bermudez, hard................	....	3.93.	.....	.....	0.75	......
Bermudez (maltha).............	....	5.87	.....	.....	....	......
Montana (maltha)..............	....	3.92	.....	.....	....	......
Mexico........................	....	1.48	.....	.....	....	......
California, Alcatraz (maltha),....	....	1.32	.....	.....	1.21	......
Gilsonite, Utah...............	....	1.79	.....	.....	0.79	......
Albertite, New Brunswick.......	....	1.20	.....	.....	0.42	......

Bromine and Iodine Absorption.—Endemann obtained the following figures for iodine absorption. No hydriodic acid was formed, hence the iodine all formed additive compounds:

	Trinidad		Mexican
	Land	Lake	
Iodine, %, in 20 hours..........	20.32	19.04	21.90

Richardson gives numerous observations of bromine absorptions. The following percentages are taken from his tables:

BROMINE ABSORPTION AND SULPHUR IN ASPHALTS, ETC.

	Sulphur	Bromine absorption	HBr.
Trinidad oil spring.................	....	29.21	18.20
		21.09	10.87
Trinidad pure bitumen...............	....	30.42	12.19
		29.99	12.58
"Petrolene" { Trinidad...............	3.25	24.46	9.54
{ Bermudez.............	3.01	19.75	8.40
"Asphaltene" { Trinidad.............	10.07	32.89	7.43
{ Bermudez.............	4.78	25.38	7.35
Bermudez, soft asphalt, middle of lake.	5.23	29.71	19.25
		24.22	15.31
Burmudez, softer asphalt, middle of lake	5.87	21.80	13.74
		32.69	18.89
Bermudez, softest asphalt, middle of lake	....	20.83	12.49
		26.78	15.74
Bermudez, oil volatilised from the asphalt......................	3.31	23.21	12.21
		23.11	14.07
Asphaltic maltha, Cal............	1.40	23.22	....
		23.73	15.31
Pedernarles refined.................	2.29	39.16	16.09
		38.54	16.83
Alcatraz liquid asphalt.............'...	1.32	25.40	16.95
		29.31	19.85
Asphalt cement from Berlin surface....	....	28.86	....
		25.89	....
Pittsburg flux.......................	4.22	....	....
Kerosene...........................	....	3.18	....
		3.62	....
Petroleum residuum, Penn............	0.60	20.80	16.40
Petroleum residuum, Penn............	0.46	22.15	15.82
Petroleum residuum, Ohio............	2.26	34.07	19.72
Petroleum residuum, Ohio............	2.07	33.41	11.23
Asphalt oil distilled *in vacuo*, 210°–220°.	1.15	23.07	9.16
Asphalt oil distilled *in vacuo*, 260°....	0.84	23.80	7.41
Asphalt oil distilled *in vacuo*, 270°....	0.55	21.42	8.82

Nature of the Hydrocarbons in Asphalt.—Richardson has studied the hydrocarbons in Trinidad and Bermudez asphalts by fractional distillations, under conditions which reduce to a minimum the liability to cracking. The lighter oils seem not to contain paraffins, olefines, acetylenes, or naphthenes, but to belong to a dicyclic series.

Artificial Asphalts.—Many attempts have been made to employ the pitches and residuums from coal-oil and coal-tar as substitutes for asphalt. Some of these paving mixtures have been laid extensively in American cities, but have almost always been unsatisfactory. A few special forms of substitute asphalts deserve notice.

"Pittsburg flux" is produced by heating coal-oil residuum with sulphur; much of the latter is converted into hydrogen sulphide and escapes, but a notable amount is retained. A tough and sticky mass is produced, which melts only at a high temperature. It differs, however, from true asphalt in several important particulars.

"Sludge asphalt" is made from the sludge-tar of the petroleum refinery by the use of sulphur, and resembles asphalt more closely than does "Pittsburg flux."

"Byerlyte" is made from the heavy petroleum oil left after the burning oil has distilled. This is heated gently for five or six days, a current of air being passed through continuously. It contains, of course, no sulphur, but the quantity of oxygen is not large.

A typical method of this kind is described as follows:

About 3.5 tons of petroleum residue of 18° B., are placed in a hooded pan and heated to 193° C., whereupon air is blown into the contents through a perforated coil for 40 hours, the volume of air admitted per hour being 5,000–6,500 cu. ft. during the first 32 hours and 3,000–4,000 cu. ft. during the remainder of the time. The mass becomes thicker and an increase in the internal heat is noticeable. The loss in weight amounts to 3.5–4%.

The changes occurring during the operation are shown in the following table, giving the composition of the mass at the different times specified.

The increased proportion of asphaltene marks the improvement of the product for the purpose in view.

	Hours			
	0	16	32	40
	%	%	%	%
Petrolene...........................	.....	90.51	74.40	73.34
Asphaltene	.....	8.03	23.46	25.14
Other organic matter	2.50	0.85	1.40	0.89
Mineral matter.......................	.....	0.61	0.70	0.63

In addition to these substitutes there is the residuum from the distillation of oils with heavy asphaltic bases. In America the products have commercial importance from both California and Texas petroleums. Being sulphur petroleums, the action of sulphur in the hydrocarbons, especially in the case of the Texas oil, produces asphaltic material in addition to that naturally occurring in the oil.

ASPHALT FLUXES.

Because of differences (largely of a physical nature) between asphalt fluxes and hard asphalts, a special series of tests is given, as suggested by Clifford Richardson.

PHYSICAL PROPERTIES.

Sp. gr., dried at 100°, 25.5°..............................
Flows, cold test...
Colour..
Odour...
Under microscope..
Flashes, °, N. Y. State oil tester.........................
Viscosity, P. R. R. Pipette ....

CHEMICAL CHARACTERISTICS.

Original substance:
    Loss, 100°, 1 hour or until dry.....................
Dry substance:
    Loss, 162.7°, 7 hours..............................
    Character of residue...............................
    Penetration of residue at 25.5°....................
    Loss, 204.4°, 7 hours (fresh sample)...............
    Character of residue ....
    Penetration of residue at 25.5°....................
Bitumen soluble in CS_2, air temperature...............
Organic matter insoluble................................
Inorganic or mineral matter.............................
Bitumen soluble in 88° naptha, air temperature, pitch .....
% of soluble bitumen removed by H_2SO_4...............
% of bitumen as saturated hydrocarbons.................
% of solid paraffins....................................
Bitumen yields on ignition:
    Fixed carbon.......................................

The methods used in making these determinations are, as a whole, the same as those described for hard asphalts with the following modifications.

Sp. Gr.—The sp. gr. on oils or fluxes is taken on the material either dried at 100°, or, if there are light oils present volatile at this temperature, on some of the oil freed from water by being swung in the centrifugal.

Heavy fluxes too dense to employ a pycnometer with are filled into an open specimen tube, 10 cm. long, 2 cm. in diameter, and holding about 27 grm. of water, even with the top, which is ground flat and parallel to the base. The weight of this volume of oil at 25.5° is compared with that of water at the same temperature. A preferable

way of obtaining the sp. gr. of very viscous tars, malthas, etc., is given under "Bituminous Road Material," page 101.

Flow Test.—Some of the oil is chilled in a large test-tube and gradually allowed to attain the temperature of the room. The point at which it will flow in the inclined tube is the flow-point.

Colour.—This is found by examining the reflection from the surface of the cold oil. It is intended to be that revealed by reflection and not by transmission light through a thin film.

Odour.—The odour can be described as that corresponding to different kinds of known petroleum in the cold or on heating.

Microscopic Examination.—The appearance of an oil that has been heated is noted under the microscope to determine the presence of material insoluble in the main mass of the oil.

Flash-Point.—The flash-point is determined in a New York State oil tester.[1] The water-bath is of course removed and the oil heated directly with a flame of a size to raise the temperature at the rate of 20° F. per minute, and a small flame from a capillary glass or metal tube is used for flashing. The flame should be applied at 5° intervals. The determination should be repeated on such oils as flash at unexpected temperatures. The water must be removed from the oil or flux before putting it in the tester cup, either by heat or by the centrifugal.

Open tests of high flashing oils are not reliable and, at best, with the closed tester a reading of 5° intervals only need be sought.

Viscosity.—A sufficiently satisfactory determination of relative viscosity for comparison of two or more oils may be obtained with a Pennsylvania Railroad viscosity pipette, heating the oils to 37.7°, or to such a temperature that they will flow freely.

At high temperatures it is necessary to surround the pipette with a water-jacket to prevent chilling.

Loss at 100°.—The water or loss of light oils at 100° is determined by weighing out 20 grm. in a crystallising dish, such as described for use in the determination of loss at 162.7° in hard asphalts, and heating in the oven described, at the temperature named, until the oil has ceased foaming. The precautions previously noted should be observed. Where oils contain a large percentage of water, this is better determined by the centrifugal method or by dilution with naphtha.

[1] See Eimer and Amend, New York, Cat. No. 6882.

Drying an oil or flux for subsequent examination is done by heating a large volume in an iron dish over a flame, with constant stirring, unless it contains much light oil, when the centrifugal method alone can be used.

Loss at 162.7° and 204.4° in Seven Hours.—Separate portions of 20 grm. of the dried material are taken for each determination and are heated to these temperatures in the manner described for solid bitumens. The residues from these oils which have been so heated are examined as under Asphalts. This is to show whether heat at such temperatures has seriously affected the bitumens.

After cooling, and weighing, the appearance of the residue is noted, especially as to whether it is smooth or granular, owing to the presence of paraffin, the temperature at which it flows, whether it pulls out to a long string or is short. If it is so hard that it does not flow except on raising the temperature above 37.7°, its consistency is determined with the penetration machine either at 37.7°, or at 25.5°. or at low temperatures.

The residue should be examined under the microscope to determine whether, owing to the nature of the fluxes, they have been at all decomposed at these temperatures with a separation of insoluble pitch, which is an evidence that the original flux must have been more or less cracked in the process of manufacture.

Total Bitumen; Inorganic Matter and Organic not Soluble; Naphtha Soluble Bitumen.—These determinations are arrived at by the methods already described for hard asphalts.

As the oils and fluxes are more easily soluble, it is unnecessary to let the solvents act on them for so long a time as in the case of hard asphalts. There is little object in using 62° naphtha with oils or fluxes, as there is too little difference between its solvent power and that of bisulphide of carbon with such materials to make it worth while. The residue insoluble in 88° naphtha, however, shows how much decomposition there has been in fluxes which have been subjected to excessive heat.

Determination of the Character of the Hydrocarbons in Fluxes.—The character of the hydrocarbons in any of the heavy oils used for fluxing purposes is determined by treatment with sulphuric acid after the method described for use with malthenes from hard asphalts.

Physical Tests on Asphalt Mastics and Paving Compositions.—

The chief tests applied on samples of the finished preparations are the tensile strength of briquettes with a machine such as is used for testing cement briquettes and the penetration test with some form of penetrometer, such as that of Bowen.

The following table shows the differences in tensile strength and penetration of some paving compositions according to Hanenschild (Deutsche Töpfer u. Ziegler Zeit., Dec., 1881).

Asphalt sample	Pressure resistance at 8° for 1 ccm.	Tensile strength in kg. per ccm.	Penetration of iron point according to Rankine at 27° mm.
Stamping asphalt Val de Travers, fresh	Crushing at 52 kg ...	26.5	6–7
Stamped Berlin Street asphalt.	Splitting apart at 93 kg.	30	7–8
Berlin "Trottoir" sheet asphalt–"Limmer."	Breaking into pieces at 65 kg.	24.38	5–6
Artificial asphalt from coal-tar, old stall floor.	Breaking in cracks at 148 kg.	29.0	1–2
I Hungarian natural asphalt, normal	Breaking in pieces at 108 kg.	25.2	4–5
II Hungarian natural asphalt, much overheated.	Quickly crushing at 109 kg.	36.75	2–3
III Hungarian natural asphalt, much overheated.	Quickly crushing at 112 kg.	36.75	4–4.5

Tests of Asphalt Lutes and Cement (suggested by Dr. Kohler, "Chemie und Technologie der natürlichen und künstlichen Asphalte): 1. Adhesive power; 2. Water-proof character; 3. Resistance to acids and alkalies; 4. Proof against plant roots; 5. Elasticity; 6. The holding of the most constant plasticity through certain limits of temperature; 7. Resistance to pressure. Fig. 3 shows the apparatus used to test the adhesive power. Mercury is allowed to flow from A into B until the weight is sufficient to pull the plates apart.

The water-proof character is shown by carrying water under pressure through terra-cotta pipes, joined together with the asphalt cement.

Roofing Papers.—For the examination of the quantity and the character of the bitumens impregnating materials, the paper is extracted with benzol or carbon disulphide. In estimating the amount of tar used, about 20% is added to the amount extracted for the free carbon that remains in the paper.

The physical tests applied are the thickness, the tensile strength, and

degree of resistance to water. The latter test is made by immersing in water for 24 hours and then noting the increase in weight.

As some papers become older they become more porous and the sand, gravel, powdered coke, etc., aids in carrying water through the body of the paper.

Action of H₂SO₄ on Bitumens.—As part of a very extensive
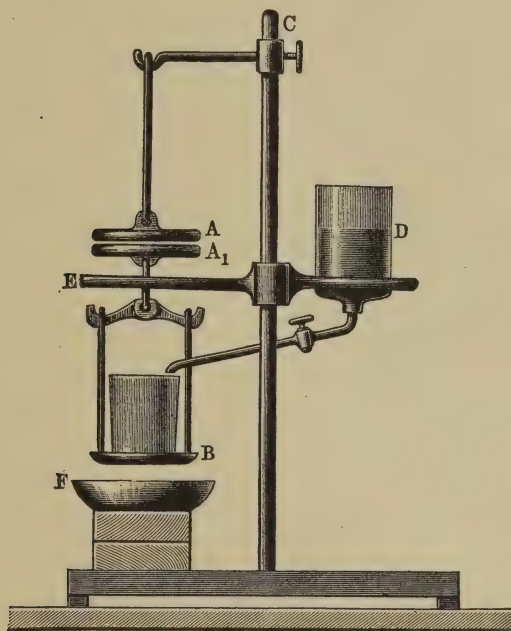
Fig. 3.

scheme of investigation of asphalt pitches, Richardson experimented with the action of sulphuric acid of different strengths on the naphtha soluble portion of asphaltic bitumens. 2 grm. of each sample were extracted with boiling 88° gasoline and this solution was shaken with 2 amounts of acid in each case, and after the acid treatment washed with sodium hydroxide and the results noted.

PER CENT. OF NAPHTHA-SOLUBLE BITUMEN UNACTED UPON BY ACIDS.

	Total bitumen	Naphtha-soluble bitumen	Percentage of total bitumens thus soluble	Percentage of naphtha-soluble bitumens unacted on by acids					
				25% NaOH	$3\frac{1}{2}$ to 1 H_2SO_4	2 to 1 H_2SO_4	1 to 1 H_2SO_4	Conc. H_2SO_4	Fuming $H_2SO_4 + SO_3$
California consolidated	66.9	47.78	71.40	84.8	71.8	67.1	64.4	54.4	4.0
Bermudez lake	96.5	67.27	69.70	80.8	80.7	80.9	78.8	38.9	19.1
Trinidad lake	57.1	34.55	60.50	90.1	89.8	87.0	79.3	38.9	19.1
Alcatraz maltha (1894)	97.9	85.19	87.00	100.0	93.7	88.4	87.0	64.2	35.7
Penn. residuum	100.0	95.68	95.71	97.4	95.5	95.6	95.5	89.5	53.3
Ohio. residuum	100.0	97.05	97.10	99.5	94.9	93.4	93.6	86.4	62.6
Russian residuum	100.0	100.00	100.00	100.0	93.6	92.7	92.2	79.3	68.8

or, calculated on another basis,

PER CENT. OF TOTAL BITUMEN REMOVED BY REAGENTS.[1]

	Total bitumen	Naphtha-soluble bitumen	Percentage of total bitumens thus soluble	25% NaOH	$3\frac{1}{2}$ to 1 H_2SO_4	2 to 1 H_2SO_4	1 to 1 H_2SO_4	Conc. H_2SO_4	Fuming $H_2SO_4 + SO_3$
California consolidated					48.7	52.1	54.0	61.2	97.1
Bermudez lake					43.5	43.6	45.1	72.8	86.7
Trinidad lake					45.7	47.3	52.1	76.5	78.6
Alcatraz maltha					17.7	23.1	24.3	44.2	69.6
Penn. residuum					8.5	8.5	8.5	14.4	49.0
Ohio. residuum					7.9	9.4	9.4	16.2	39.2
Russian residuum					6.4	7.3	7.3	20.7	31.2

[1] More thorough extraction would have increased these percentages in some cases.

BITUMINOUS ROAD MATERIALS.

In the last 2 or 3 years this branch of analytical work has become necessary, due to the large consumption of materials used for making asphalt and tar macadam roads. The bituminous material should have the maximum cementing strength and sufficient non-volatile constituents. The following tests have been selected by Clifford Richardson and C. N. Forrest as best adapted to meet specifications.

Sp. Gr.—The sp. gr. of light oils is determined with a pyknometer or a Westphal balance at 25°. Heavy substances, too viscous for test by the above instrument, are examined by the Kirschbraun method:

Take a test-tube about half an inch in diameter and cut it off to give a 1 3/4 inch by 1/2 inch tube. Flare it out to carry a fine wire. Put about 10 grm. of the oil or asphalt into it, and suspend it into an oven to remove air bubbles and drive off the water. Cool and weigh accurately in air and immerse in distilled water at 25° to a fixed mark on the wire and weigh. Previous to filling the tube with the sample, determine its weight carefully in air and in water at 25°, immersed to the fixed mark. These weighings give the weights of the tube alone in air and in water, and the combined weights of the tube and sample in air and water.

The gravity is calculated in this way, representing

Weight of tube in air.................................... a
Weight of tube and sample in air......................... b
Weight of tube in water................................. c
Weight of tube and sample in water............. .... d

$$\text{Sp. gr.} = \frac{\text{Wt. in air of sample}}{\text{Loss of wt. in water}}.$$

in this case becomes

$$\frac{b-a}{(b-a)-(d-c)} \cdots\cdots\cdots (1)$$

When the gravity of the sample is less than unity the second expression in the denominator is a negative $(d-c)$ quantity and is added to the original weight of the sample $(b-a)$, inasmuch as the buoyancy of the sample will overcome its own weight, and, to a certain extent, will also reduce the weight of the tube in water, making c greater than d.

The formula in this case may be also expressed so:

$$\frac{b-a}{(b-a)-(c-d)} \cdots\cdots\cdots (2)$$

When the gravity of the sample is greater than unity, d will be greater than c and the first formula applies without confusion. As an example, take a blown oil, the gravity of which was determined in Richardson's laboratory according to this method:

Weight of tube in air............................ a = 4.7870
Weight of tube and sample in air................ b = 16.7900
Weight of tube in water, 25°..................... c = 2.8565
Weight of tube and sample in water.............. d = 2.6425

by formula (2)

$$\text{Sp. gr.} = \frac{16.7900 - 4.7870}{(16.7900 - 4.7870)(2.8665 - 2.6425)} = \frac{12.0030}{12.2170} = .9817$$

This may seem arther complicated at first, but it will be noticed that the factors a and c are constants, which can be used for the same tube without change, and the calculation becomes very simple after a few trials.

The advantages of the method are in doing away with the inconveniences of handling a large amount of oil, and the ease with which air bubbles can be removed. Of course, it can be used only with oils which are viscous enough to be retained in the tube when under water.

Flash Test.—The flash-point is determined in a New York State closed oil tester. The water-bath is, of course, removed and the oil heated directly with a flame of a size to raise the temperature at the rate of 6.6° per minute, and a small flame from a capillary glass or metal tube is used for flashing. The flame should be applied at 5° intervals. The determination should be repeated for such oils as flash at unexpected temperatures.

The water must be removed from the oil or flux before putting it in the tester cup, either by heat or by the centrifugal.

Bitumen Soluble in Carbon Disulphide, or Total Bitumen.— 1 grm. of the dry material is weighed out and introduced into a 200 c.c. Erlenmeyer flask of Jena glass, and covered with about 100 c.c. of carbon disulphide. It is then set aside for at least 5 hours, or overnight, at the temperature of the laboratory. In the meantime, a Gooch crucible is prepared with an asbestos felt and weighed. This Gooch crucible is of a special form, with a large filtering surface. It holds 30 c.c., is 4.4 cm. wide at the top tapering to 3.6 cm. at the bottom, and 2.6 cm. deep. This is much better for percolation work than the usual narrow form of Gooch. The felt is made by beating

up long-fibre Italian asbestos in a mortar, and suspending the finer particles in water and quickly pouring off from the coarse particles. Too much of the latter should not be removed, or the felt will be too dense. The decanted asbestos and water are shaken up, and what is found to be a proper amount poured into the crucible, which has, in the meantime, been attached to a vacuum filtering flask by the proper glass and rubber connections. As soon as the asbestos has somewhat settled, the vacuum-pump is started, and the felt firmly drawn on the bottom of the crucible. It is then dried, ignited, and weighed.

After standing a proper time, the disulphide is decanted very carefully upon the filter, which is supported in the neck of a wide-mouthed flask and allowed to run through without suction. The flask, after being tipped to pour the first portion, is not again placed erect, in order to avoid stirring up any insoluble material, but is held at an angle on any suitable base, such as a clay chimney. After all the disulphide has been decanted, more is added and the insoluble matter shaken up with it. This is allowed to settle and decanted as before, the insoluble matter being finally brought on the filter and washed with the solvent until clean. The excess of disulphide is allowed to evaporate from the Gooch crucible at the temperature of the room. It is then dried for a short time at 100° and weighed. The loss of weight is the percentage of bitumen soluble in carbon disulphide.

In the meantime, the filtrate, transferred to a platinum dish, is placed in a good draught and lighted. When all the bisulphide has burned, the bitumen remaining in the dish is burned off over a lamp and the mineral residue, which escaped the filter, is weighed. The weight is added to that of the Gooch crucible or subtracted from the % of bitumen found without its consideration, as a correction. Care must be used in this method of procedure that the solvent does not creep over the sides of the crucible and that the outside is free from bitumen before weighing. In order to avoid this, the crucible is preferably supported in the neck of a flask with three constrictions, the neck extending above the top of the crucible and the latter being covered with a watch-glass.

Naphtha-soluble Bitumen.—1 grm. of the substance is weighed into a 200 c.c. Erlenmeyer flask, covered with naphtha and allowed to stand, as in estimating total bitumen; in fact, the entire process is the same, with the exception that one or two precautions must be observed. It is well not to attempt to break up any lumps with a stirring

rod, as the substance, especially the softer asphalts, may then adhere to the rod or flask, and be difficult to detach. It may also be necessary to treat the substance with several portions of the solvent. No heat is applied at any time in the process, and the filtration is made without suction. The filtrate containing the naphtha-soluble bitumen is evaporated spontaneously in a crystallising dish until the naphtha is expelled. At 25° the residue in the dish is tested with the fingers to ascertain whether it is merely oily or of a sticky and adhesive character.

Residual Coke or Fixed Carbon.—This determination should be made according to the method described for coal in the *J. Amer. Chem. Soc.*, 1898, **20**, 481–5.

The residue minus the small impurity of ash in the pure bitumen is the fixed carbon, which should be calculated to 100% with the volatile hydrocarbons, excluding the inorganic matter.

FIG. 4.

Paraffin Scale.—The distillation method is employed for this purpose.

100 grm. of the oil is distilled rapidly in a 6-oz. retort to dry coke. 5 grm. of the well-mixed distillate is treated in a 2-oz. flask with 25 c.c. of ether (for anesthesia); after mixing together thoroughly, 25 c.c. absolute alcohol is added, and the flask packed closely in a freezing mixture of finely-crushed ice and salt for at least 30 minutes. Filter off the precipitate quickly by means of a suction pump, using a No. 575 C. S. & S. 9-cm. hardened filter, cooled by the above freezing mixture in a suitable apparatus (see Fig. 4).
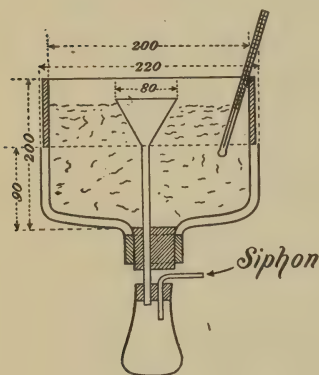
Rinse and wash the precipitate with 1 to 1 (absolute) alcohol and ether mixture, cooled to 0° F., until free from oil. 50 c.c. of the wash solution is usually sufficient. When sucked dry, remove the paper, transfer the waxy precipitate to a small glass crystallising dish. Dry on a steam-bath, and determine the weight of paraffin scale remaining in the dish.

$$\frac{\text{Wt. of paraffin}}{\text{Distillate taken}} \times \%\frac{\text{original}}{\text{distillate}} = \% \text{ paraffin scale.}$$

Viscosity.—The viscosity of bituminous road material is determined in the Engler viscosimeter at any temperature desired. The full quantity, 250 c.c. is placed in the apparatus and raised to the temperature at which it is desired to make the test. 100 c.c. is then permitted to flow into a graduated flask of the above capacity, and the time of the flow in seconds is noted. The result may be expressed either in seconds or by ratio compared with the time of flow of a similar quantity of water at 25°.

Road binders should be too viscous for testing in the Engler apparatus at temperatures below 121.1° to 176.6°, and to determine the consistency of such materials at normal or slightly elevated temperatures the New York Testing Laboratory float apparatus is employed.[1]

The apparatus, which is made by Howard and Morse, Brooklyn, N. Y., consists of two parts, an aluminum float or saucer, and a conical brass collar. The two parts are made separately for reasons of economy, so that 1 or 3 of the floats will be sufficient for an indefinite number of brass collars.

In using the apparatus, the brass collar is placed upon a brass plate, the surface of which has been amalgamated, and filled with the bitumen under examination, after it has been softened sufficiently to flow freely by gentle heating.

The collar must be completely filled, and as soon as the bitumen has cooled sufficiently to handle the collar is placed in ice-water at 5° for 15 minutes. It is then attached to a float and immediately placed upon the surface of the water, which is maintained at 32.2° or any other temperature desired.

"As the plug of bitumen in the brass collar becomes warm and liquid, it is gradually forced out of the collar, and as soon as the water gains entrance to the saucer the entire apparatus sinks below the surface of the same.

"The time, in seconds, elapsing between placing the apparatus on the water and when it sinks, is determined most conveniently with a stop-watch, and is considered as the consistency of the bitumen under examination."

Cementing Value.—Petroleum oils have very feeble, if any, cementing value. Materials requiring a high temperature to flow freely will not adhere to cold road metal. To determine these properties, the metal under examination is heated to the temperature at which it

[1] Eng. Rec., Vol. 59, p. 584, May 1, 1909.

is used in practical work, and a portion is then flowed over the surface of a slab of marble or glass, 4″x5″x1″ thick. After standing 24 hours at 25°, the film upon the stone must be decidedly sticky when tested with the fingers, and must adhere to the stone so that it cannot be pulled off.

Volatile Substances.—100 grm. of the material is placed in a 6-oz. tubulated glass retort, with the bulb of an accurate thermometer in the same. Heat is now applied so that the temperature rises at the rate of 10° per minute to 700° F. The distillate, if any, is regarded as the amount of volatile substances in the material. The residue is examined by the New York Testing Laboratory float for consistency, and compared with the results obtained upon the original material by this test.

PETROLEUM AND SHALE PRODUCTS.

The parallel products obtained by the distillation of crude petroleum and the oil or tar from bituminous shale (page 161) present a marked similarity in general character, though differing notably in certain respects. As a rule, the treatment of petroleum is a much simpler operation than the manufacture of marketable products from crude shale oil, but, broadly speaking, the same method of treatment is applied to both of the raw materials. The process employed consists essentially in fractional distillation, and treatment of the separate fractions successively with sulphuric acid and caustic soda, to remove bodies of acid and basic character and to destroy the less stable hydrocarbons. The less volatile portions deposit paraffin wax on cooling. The following table shows in parallel columns the character and quantities of the products obtained in first-class works from crude American petroleum of 0.800 sp. gr. and Scotch shale oil produced at the works of the Broxburn Oil Company:

Products	From petroleum		From shale oil	
	Sp. gr.	Percentage	Sp. gr.	Percentage
Cymogene and rhigolene	.590 to .625	very small	....	very small
Gasolene	.636 to .657	1.0 to 1.5		
"C" naphtha ("benzin-naphtha")	.700	5 to 1c	0.730	
"B" naphtha	.714 to .718	2.5		5
"A" naphtha ("benzin")	.725 to .737	2.0 to 2.5		
Kerosene or burning oil	.802	50 to 70	0.800 to .810	37
Lubricating oil	.875	2.5 to 17	0.885	17
Paraffin wax	....	2	....	13
Coke, gas, and loss	....	8 to 10	....	28

The yield of burning oil from any sample of petroleum may be increased nearly 20% with corresponding diminution of heavier products by a modification of the distillation by which the hydrocarbons of higher b. p. are changed by dissociation into bodies of lower b. p. This process, technically known as "cracking," was discovered by accident in an American refinery about 50 years ago, and is now generally adopted since an increase in the burning oil is the most valuable result to the refiner. The chemistry involved in the change is not thoroughly understood. It is carried out in practice by arranging the distilling apparatus so that the hydrocarbons are condensed and fall back in drops upon the much hotter body of the liquid in the still. By this action the condensed oils become overheated and changed. Burning oils obtained by this method are different from, and somewhat inferior to, those produced by normal distillations, but the process, as noted above, is very much in vogue.

The Abruzzo bitumen is said to yield on distillation:

	%	Sp. gr.	Flashing point, °
Burning oil............................	15	0.850	54.5°
Intermediate..........................	33	0.945(?)	121.1°
Lubricant.............................	16½	0.990(?)	157.2°

The products from Russian petroleum are very different in both density and percentage from those yielded by the American oil (see pages 108, 128 and 129). Rangoon tar of 0.885 sp. gr. gives, on an average, the following proportions of refined products: Burning oil (sp. gr. 0.832), 30%; lubricating oil (sp. gr. 0.901), 51%; and paraffin scale (melting at 51.4°), 10.7%.

The products obtained by the distillation of ozokerite have already been described.

The number of products into which the more volatile portions of shale oil and petroleum are fractionated varies considerably according to the practice of the works, but gasolene and the more volatile products are obtainable from shale oil equally with petroleum. The only commercial product obtainable from petroleum having no analogue among the products from shale oil is the substance known as vaseline. Sadtler (*Ind. Org. Chem.*) quotes the following table from *Wagner's Jahresbericht*, 1886, for the percentage yields of petroleum distillation on the large scale:

Crude oil	Benzin and volatile oils	1st quality burn. oil	2d quality burn. oil	Residuum
Pennsylvania....................	10 to 20	60 to 75		5 to 60
Galicia........................	3 to 6	55 to 65		30 to 40
Alsace.........................	....	35 to 45		55 to 60
Roumania......................	4	60 to 70		25 to 35
Baku (Bibi-Eibat)..............	10.5	40	13.5	36
Baku (Balakhan)...............	5 to 6	27 to 33	5.6	50 to 60

The more volatile products from petroleum are briefly described on page 111. The similar fractions from shale oil closely resemble the petroleum products in their physical characters, but they contain a much larger proportion of olefines. This chemical distinction had been traced by Allen in each of the parallel products from American petroleum and shale oil, and is the cause of some curious differences in the behaviour of these substances as solvents and with chemical reagents.

The following table gives a general idea of the chemical composition of the leading commercial hydrocarbon products derived from bituminous shale and American petroleum. Of course, the quantitative composition is liable to considerable variation, and hence must not be interpreted too strictly. The general and analytical characters of the products named in the table are described in the succeeding sections. The hydrocarbons from distillation of coal do not admit of parallel comparison with those from petroleum and shale.

Product	Bituminous shale	American petroleum
Naphtha..............	At least 50 to 60% of heptene and homologues. The remainder as paraffins. No trace of aromatic hydrocarbons.	At least 75% of heptane, and homologues. The remainder apparently olefines, with distinct traces of aromatic hydrocarbons.
Kerosene, or burning oil	50 to 80% or more of the higher olefines. The remainder paraffins.	50 to 80% of higher members of the methane series. The remainder chiefly olefines.
Lubricating oil........	Chiefly olefines, with some polymerised members of the acetylenes.	A large proportion of higher olefines, but less than in corresponding shale product.
Vaseline..............	No such product.........	Chiefly higher (iso-?) paraffins of low m. p.
Paraffin..............	Paraffins..............	Paraffins.

From this table it will be seen that while the paraffins are conspicuous in American petroleum, shale products are remarkable for their richness in olefines. In consequence of this peculiarity of constitution, concentrated nitric and concentrated sulphuric acid act far more vigorously on shale products than on the parallel products from petroleum, and the proportion of paraffins given in the above table really represents the percentage by measure of hydrocarbons which withstand a consecutive treatment with nitric acid of 1.45 sp. gr. concentrated sulphuric acid, fuming sulphuric acid, and sodium hydroxide. Russian petroleum behaves with reagents much like American petroleum, but consists largely of cyclic hydrocarbons (naphthenes).

A much more satisfactory method, and one which gives fairly constant results, is based on the fact that paraffins and naphthenes do not react with bromine, while the hydrocarbons of most other series take it up freely, forming additive or substitution products (page 110).

The following table shows the results obtained by Allen as to the action of bromine on various representative commercial products from shale, and American and Russian petroleum. The shale products were furnished by Mr. R. Tervet; those derived from American petroleum (with the exception of the gasolene and vaseline) were furnished by Mr. J. Merrill, of Boston, Mass.; and the Russian petroleum products by Messrs. Ragosine & Co. The solution of bromine in dry carbon disulphide was allowed to act on the dry oil for from 15 to 30 minutes in the dark, when potassium iodide was added and the liquid titrated with decinormal thiosulphate. After titration the solution was filtered, and the aqueous liquid titrated with standard alkali hydroxide and litmus. From the amount used, the proportion of hydrobromic acid formed was ascertained, and from this the bromine existing in that form was calculated.

From these results it will be seen that there is in every case a marked difference between the proportion of bromine assimilated by any of the shale products and the quantity which combines with the parallel product from American petroleum, especially in the lighter fractions. It is evident, however, that the results must not be interpreted too strictly, for an oil which was obtained by "cracking" would be richer in olefines, and hence would show a higher bromine-absorption than one of another kind.

The results yielded by the products from Russian petroleum are

still more striking, though other samples of kerosene have shown higher absorptions (*e. g.*, 15%) than those given in the table.

The following determinations by Mills and Snodgrass were made by the process described in Vol. 2, page 26.

Product	Sp. gr.	Bromine-absorption
Lubricating shale oil......................	0.860	22.2
Lubricating shale oil......................	0.870	20.6
Lubricating shale oil......................	0.890	12.6
Lubricating shale oil......................	0.900	11.7

Description of substance	Sp. gr. at 15.5°	Grm. of bromine reacting with 100 grm. of sample	Bromine as HBr per 100 grm. of sample
Gasolenes.			
From shale.........................	0.665	62.2	1.1
From American petroleum............	0.650	17.9	3.1
Naphthas.			
Shale naphtha......................	0.720	67.2	4.0
C. naphtha from American petroleum..	0.706	18.3	....
Burning Oils.			
From shale.........................	0.813	51.3	3.0
From American petroleum	0.800	34.8	....
From Russian petroleum.............	0.821	2.0	0.1
Intermediate Oils.			
From shale.........................	0.850	48.2	....
"Mineral sperm oil" (American petroleum).........................	0.847	32.3	....
"Pyronaphtha" (Russ. petr.)..........	0.868	1.9	0.1
Lubricating Oils.			
From shale.........................	0.890	25.6	5.8
Cylinder oil (from shale).............	0.890	11.0	....
From American petroleum (heavy spindle oil).......................	0.900	11.7	....
From Russian petroleum.............	0.904	4.9	0.8
"Champion oil" (Amer. petr.).........	0.911	9.9	0.8
Cylinder oil (Russian petr.)..........	0.909	5.8	0.6
Vaselines.			
From American petroleum (Chesebrough Co.).......................	0.856	11.3	1.8
From Russian petroleum.............	....	1.7	0.3
Paraffin Waxes.			
From shale (m. p. 52°)..............	....	1.7	0.5
From petroleum (m. p. 54°)..........	....	0.9	0.2

These results are interesting as showing the diminution of the bromine-absorption with the increase in the density of the oil, and presumably with the mean molecular weight of its constituents.

MINERAL NAPHTHA.

Petroleum Spirit. Shale Naphtha.

These names are employed to signify generally the more volatile fractions obtained by the distillation of petroleum or shale oil. By some manufacturers the products from American petroleum are further divided into fractions distinguished in following table. B. Redwood gives the following classification of the more volatile portions of American petroleum: 0.637, rhigolene or cymogene for surgical purposes; 0.642 to 0.648, gasolene for air-gas machines; 0.680, boulevard gas fluid for street naphtha lamps; 0.690 to 0.707, prime city naphtha (benzolin) for sponge-lamps, etc.; 0.729, benzin, for oil cloth and varnish making.

Commercial name	Degrees Baumé	Sp. gr.	Composition
Cymogene......................	108	0.588	Consists chiefly of tetrane, C_4H_{10}.
Rhigolene..................	94 to 92	0.625 to 0.631	Consists chiefly of pentane and isopentane, C_5H_{12}.
Gasolene (Canadol)..........	95 to 80	0.622 to 0.666	Consists chiefly of hexane, C_6H_{14}, and isohexane.
C. naphtha............ Benzin-naphtha.........	76 to 70	0.680 to 0.700	
B. naphtha..............	66 to 65	0.714 to 0.718	
A. naphtha........... Benzin................	59 to 58	0.740 to 0.745	

(Petroleum ether: Rhigolene, Gasolene (Canadol). Petroleum spirit, or benzolin: C. naphtha / Benzin-naphtha, B. naphtha, A. naphtha / Benzin.)

Pentane.—With the exception of methane, which exists in a fairly pure state in natural gas, pentane is perhaps the only other single constituent of petroleum that is obtained from it and used commercially. Normal pentane boils at 36.3°, and so can only be kept at ordinary temperatures

in sealed cans, etc.   Pentane is burned in the pentane lamp used in photometry.   According to C. O. Bond (*J. Frank. Inst.*, Mar., 1908, 189–209) the following methods are adopted in preparing pure pentane and testing it.

Light American petroleum, such as is known as gasoline and used for making air gas, is to be further rectified by 3 distillations, at 55°, 50° and 45° in succession.   The distillate at 45° is to be shaken up from time to time, during 2 periods of not less than 3 hours each, with 1/10 its bulk of (1) strong sulphuric acid, and (2) a solution of sodium hydroxide.   After these treatments it is to be again distilled, and that portion of it to be collected for use which comes over between the temperatures of 25° and 40°.   It will consist chiefly of pentane, together with small quantities of lower and higher homologues whose presence does not affect the light of the lamp.

Testing Pentane.—The density of the liquid pentane at 15° should not be less than 0.6235 nor more than 0.626 as compared with that of water of maximum density.   The density of the pentane when gaseous, as compared with that of hydrogen at the same temperature and under the same pressure, may be taken.   This is done most readily and exactly by Gay Lussac's method, under a pressure of about half an atmosphere, and at temperatures between 25° and 35°.   The density of gaseous pentane should lie between 36 and 38, hydrogen being taken as 1.

Any admixture with pentane, of hydrocarbons belonging to other groups and having photometric value—such as benzene or amylene— must be avoided.   Their presence may be detected by the following test: Bring into a white stoppered glass bottle of from 80 c.c. to 100 c.c. capacity, 10 c.c. of nitric acid, sp. gr. 1.32 (made by diluting pure nitric acid with half its bulk of water).   Add a few drops of a dilute solution of potassium permanganate, sufficient to give to the acid a full and permanent pink colour.   Pour into the bottle 50 c.c. of the sample of pentane, and shake strongly from time to time during 5 minutes. If no hydrocarbons other than paraffins are present, the pink colour, though somewhat paler, will still be distinct.   If there is an admixture of as much as 0.5% of amylene or benzene, the colour will have disappeared.

Because of the growing use of petroleum spirit of different densities for automobile use and extraction purposes, it is more necessary than ever before to examine gasolines and naphthas by distillation.

A dephlegmator is generally used to more effectually separate the constituents.

In England and America the dephlegmators designed by Young and Tervet are much used, while in Germany the Glinsky-Le Bel form is perhaps most used. From 250 c.c. to 1 litre is used in the distillation and with benzin fractions are taken up to 50° from 50 to 100, 100 to 120, 120 to 150, 150 upwards.

With lighter cuts, such as would be termed gasoline and with crude first-run naphtha different fractions might be taken. With the use of a dephlegmator one distillation is sufficient.

The term ligroïn is sometimes used to indicate a petroleum product boiling between 70° and 120°, and having a sp. gr. between 0.685 and 0.690. All the products from Russian petroleum are of greater sp. gr. than the parallel products from the American oil.

A rule of the New York Product Exchange defines petroleum naphtha as "water-white and sweet, and from 68° to 73° Baumé" (=0.707 to 0.690 sp. gr.).

The employment of the terms "benzolin," benzine," and "benzin" to denote the more volatile fractions obtained on distilling petroleum or shale oil has caused great confusion between the products so called and benzene, C_6H_6, the leading constituent of coal-tar naphtha. This confusion has been increased by the intentional substitution, partial or complete, of one product for the other. Methods for distinguishing petroleum spirit from coal-tar naphtha and for analysing mixtures of the two are described later.

Petroleum spirit (which would be preferably called "light petroleum") consists of a mixture of homologous hydrocarbons of the paraffin series, with smaller quantities of olefines, etc., and traces of cyclic hydrocarbons. The relative proportions of the several constituents vary according to the b. p. and density of the sample, pentane and hexane being the chief constituents of the lighter and more volatile fractions, such as gasolene, while heptane is the leading constituent of the denser kinds, such as commercial benzolin, in which octane and even higher homologues are also present. Petroleum spirit is a thin, colourless liquid, having, when refined, a peculiar but not unpleasant odour. It gives off inflammable vapour at ordinary temperatures, and rapidly evaporates. It is said to absorb oxygen from the air. It is insoluble in water, but dissolves in about six parts of rectified spirit. It has considerable solvent properties. The lighter forms especially

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dissolve caoutchouc, asphalt, and, with less facility, colophony, mastic, and dammar resin. The heavier form (sp. gr. 0.745) is said not to dissolve resins. Petroleum spirit dissolves, in all proportions, the fixed oils of almond, olive, rape, linseed, croton, cod-liver, palm, coconut, theobroma, and lard. It does not dissolve castor oil, but the latter liquid dissolves its own volume of petroleum spirit (Vol. 2, page 163). Petroleum spirit also dissolves naphthalene, paraffin, wax, and many similar bodies, and is miscible in all proportions with amyl alcohol, ether, chloroform, benzene, oil of turpentine, creosote, and cresols, but not with phenol.

Petroleum spirit of 0.716 sp. gr. at 15° has a heat of combustion of 11,157 calories per Kg., or 20,083 British thermal units per pound avoirdupois.

Purified Petroleum Benzin (Benzinum Purificatum of the United States Pharmacopœia).—Add 60 c.c. of sulphuric acid to 550 c.c. of water, and when the mixture has become cold, pour it into a bottle having the capacity of about 2 litres. Add 8 grm. of potassium permanganate and agitate until it is dissolved, then add the petroleum benzin, in 4 portions of 250 c. c. each, shaking the liquid after each addition. Allow the liquids to remain in contact for 24 hours, shaking the bottle at frequent intervals; then decant the petroleum benzin into another bottle of the same capacity, and having dissolved 2 grm. of potassium permanganate in 240 c.c. of water, in which 2 grm. of sodium hydroxide has previously been dissolved, mix the liquids and agitate the mixture frequently during several hours, then decant, repeat the washing with water, and again decant the purified petroleum benzin.

On evaporating 10 c.c. of purified petroleum benzin from a piece of clean filter-paper, no greasy stain should remain, and the odour should not be disagreeable or notably sulphuretted; no residue should be left upon evaporating purified petroleum benzin from a warmed dish (absence of heavy hydrocarbons).

When it is boiled for a few minutes with 0.25 its volume of spirits of ammonia and a few drops of silver nitrate T. S., the liquid should not turn brown (absence of pyrogenous products and sulphur compounds).

Purified petroleum benzin should have an ethereal or faint petroleum-like odour, and should respond to the tests given under Benzinum.

The tests of the U. S. P. for Benzinum are: Sp. gr., 0.638 to 0.660 at 25°; soluble in 6 pts. of alcohol; b. p., 450° to 60°. If 5 drops of

petroleum benzin be added to a mixture of 40 drops of sulphuric acid and 10 drops of nitric acid, in a test-tube, the liquid warmed for about ten minutes, and then set aside for half an hour, or diluting it in a shallow dish with water, it should not evolve the bitter almond like odour of nitrobenzene (difference from, and absence of, *benzene*).

The "petroleum benzin" of the German Pharmacopœia is the colourless, non-fluorescent portions of petroleum, having a sp. gr. of 0.640 to 0.670, and distilling almost entirely between 55° and 75°. On adding 2 c.c. of this liquid to a cold mixture of 1 c.c. of sulphuric acid and 4 c.c. of fuming nitric acid and shaking, no appreciable colour and no odour of bitter almonds should be produced.

The British Pharmacopœia (1898) defines "petroleum spirit" to be a derivative of petroleum, boiling between 50° and 60°, and with a sp. gr. between 0.670 to 0.700.

Petroleum spirit is liable to contain impurities, which unfit it for certain uses. If of good quality, it will leave no odour when evaporated on the hand, and when evaporated in a porcelain basin heated over boiling water, will leave no oily residue of *heavy hydrocarbons*. Boiled for a few minutes with alcohol and a few drops of ammonia, a brown colouration produced on subsequently adding silver nitrate solution indicates *sulphur compounds*, which render the sample unfit for use as a turpentine substitute, as it will be liable to discolour white paints. When petroleum spirit is agitated with warm water, the water after separation should be perfectly neutral in reaction, and should give no cloud with barium chloride (absence of *sulphuric acid* and *sulphonates*).

The sp. gr. is best determined by means of a hydrometer at 15° or if at another temperature, allowance is made according to the following table:

Sp. gr.	Correction for each degree
0.700 to 0.720..........................	0.000820
0.720 to 0.740..........................	0.000818
0.740 to 0.760..........................	0.000800
0.760 to 0.780..........................	0.000790
0.780 to 0.800..........................	0.000780

Water cannot exist in notable quantity in petroleum spirit without rendering the liquid milky. If present to an extent sufficient to be thus visible, the liquid is rendered unfit for burning in sponge lamps,

etc. The water may be removed by prolonged subsidence, or more rapidly and perfectly by agitating the sample with a little dry plaster of Paris.

	Petroleum spirit	Shale naphtha	Coal-tar naphtha
Chemical composition.	Contains at least 75 % of paraffins, principally heptane, the remainder apparently olefines, with traces of aromatic hydrocarbons	Contains at least 40 to 50% of olefines, principally heptene; the remainder paraffins. No trace of aromatic hydrocarbons.	Consists almost wholly of benzenes. A small percentage of open-chain hydrocarbons in some samples.
Sp. gr. at 15°.....	0.700	0.718	0.876
Chiefly distils between........	65° and 100°.	65° and 100°.	80° and 120°.
Solvent action on coal-tar pitch.	Very slight action; liquid but slightly coloured even after prolonged contact.	Behaves similarly to petroleum spirit.	Readily dissolves pitch, forming a deep brown solution.
Behaviour on shaking 3 volumes of the sample at 20° with 1 measure of fused crystals of absolute phenol.	No apparent solution; the liquids are not miscible, but set to a mass of crystals when cooled slightly below 0°.	The liquids form a homogeneous mixture, often setting to a mass of crystals at 18° to 20°.	The liquids form a homogeneous mixture.
Reaction with bromine in the cold.	Combines with 10 to 20% of its weight of bromine.	Combines with upward of 60% of its weight of bromine.	Reacts slowly with a considerable proportion of bromine.

Benzin for Degreasing.—For this purpose it is desirable to choose one that does not contain a large percentage of very low boiling or a large amount of high boiling constituents. In the first case too much is lost by evapouration and in the second too much heating is required to expel all of the solvent from the fat, and the fat is also injured thereby. Most of the benzin should distil between 80° and 110°, 95° being considered the ideal mean.

Analyses of these oils consists in making distillation records with 100 c.c. of benzol in a suitable dephlegmator and noting the amount of distillate between each 10° intervals of temperature, starting at 70° and running to 110°. The rate of distillation is about 1 drop per second.

Shale naphtha, which is the lighter and more volatile portion of

the oil obtained by the distillation of bituminous shale, is a product very similar to petroleum spirit in most of its properties and uses. Allen found, however, that the shale naphtha presents certain differences, which are due to a much larger proportion of olefines than exist in petroleum naphtha. The table on page 116 exhibits concisely these differences, and compares the characters of a sample of coal-tar naphtha with specimens of similar products from shale and American petroleum. Variation in minor details will be met with in different samples from similar sources. (See Crude Shale Oil, page 16.)

MINERAL BURNING OIL.

Kerosene. Coal Oil.

Under these names, and others more fanciful and less appropriate, are classed the fractions of petroleum and shale oil which are suited for burning with a wick. The petroleum product is often broadly described as "refined petroleum," and that from shale oil as "paraffin oil," but the latter name is often popularly applied to heavier oil from petroleum. The name "kerosene" is a contraction of *keroselain*, or "wax oil," and was originally a trademark adopted for a certain patented fraction of coal oil. The term has now been adopted as the most convenient to apply to mineral burning oils generally.

Kerosene is a colourless or yellowish oily liquid, often possessing a well-marked blue fluorescence. It has a characteristic taste and smell which it imparts to water, though practically insoluble in that liquid. It is only moderately soluble in alcohol, but is miscible in all proportions with ether, chloroform, benzene, petroleum spirit, volatile oil, and fixed oils, with the exception of castor oil. It dissolves phosphorus, sulphur, iodine, camphor, many resins, waxes, fats, and softens india-rubber.

The commercial varieties of mineral burning oil are very numerous, and hence the physical characters are not very constant.

The sp. gr. of ordinary American kerosene is about 0.790 to 0.800, the parallel product from shale oil being 0.800, and from Russian (Baku) petroleum 0.822. Burning oils of higher densities are also largely manufactured, and are well adapted for special purposes.

The following are the characters and special applications of certain other varieties of mineral burning oils:

Colzarine Oil.—Sp. gr. about 0.838; fire-test 121° (250° F.).   Quite odourless, pale amber; specially intended for burning in "moderator" and "carcel lamps."

Cazeline Oil.—Sp. gr. 0.805; fire-test 62.2° (144° F.).   Limpid, with scarcely a trace of colour, and very light odour.

Mineral Sperm Oil.—Sp. gr. 0.829 to 0.847.   Abel flash-point 115.5° (240° F.); fire-test about 148.8° (300° F.).   Specially adapted for lighthouse and locomotive lights.   Its use is compulsory on some of the American railroads, and it is also extensively employed on board ship.   "Mineral colza oil" and "mineral seal oil" are similar products.

Belmontine Oil.—Obtained by distillation of Rangoon tar or Burmese petroleum with superheated steam.   Sp. gr. 0.847; fire-test 56.6° (134° F.).   Though heavy, the oil has but little viscosity, and will rise through a long wick.   The flame is very white, and of high illuminating power.

Pyronaphtha is a product from Russian petroleum somewhat similar to mineral sperm oil.   It has a density of 0.858 to 0.869, a fire-test of 294° (265° F.), and a flash-point by the Abel test of 96.1° (205° F.) to 121.1° (250° F.).   (See also page 46.)

Solar oil is a name commonly applied in Russia to an intermediate oil of about 0.860 sp. gr., and flashing at about 104.4° (220° F.) by the Abel test.

Various fanciful names have been given to petroleum and shale products employed for illuminating purposes.   It is often pretended that some process has been used to remove dangerously inflammable constituents.   All such products come under the legal definition of "petroleum" (see pages 126 and 127), and the "flashing-point" is a satisfactory test of their nature.

The photogene oil from shale resembles refined petroleum in all essential physical respects; but, when examined by the bromine process, the shale product is found to contain a smaller percentage of paraffins and more olefines than is the case with petroleum.   Some samples of shale photogene contain only 5 or 6% of paraffins.   The author has frequently found that when 3 measures of petroleum kerosene were shaken with one of fused crystals of absolute phenol, the latter gradually assumed a dark violet, and ultimately a black, colour, but the reaction is not invariably produced; and no such reaction was observed to occur with burning oil from shale.   The mixture of petroleum kerosene and phenol becomes turbid at 42° to 49°, but

the shale oil mixture remains clear till the temperature has fallen to about 25°.

Assay of Mineral Burning Oil or Kerosene.—Good kerosene should be water-white or light yellow, with or without blue fluorescence. A decided yellow indicates imperfect purification. If kept in clear glass bottles, exposed to light, it often acquires a yellow colour, becomes ozonised, and bleaches the cork. Kerosene so changed will not burn well. The odour should be faint and not disagreeable. When agitated with an equal volume of sulphuric acid of 1.53 sp. gr., the colour ought to become lighter rather than darker. The sp. gr. is rarely less than 0.795, except in certain water-white oils, or *ordinarily* above 0.810 in the case of American, or 0.823 in the case of Russian oil, but kerosene from different sources, and intended for different special purposes (see page 118), varies considerably in this respect, and hence the indication afforded by the density must not be interpreted too strictly. The absence of an objectionable proportion of very volatile constituents or "naphtha," as indicated by the flashing point, and the absence of a large proportion of "tailings" or heavy oil, as indicated by fractional distillation, are the most important characters in judging of the quality of a sample of kerosene. The rules of the New York Produce Exchange provide that refined petroleum or kerosene for contract purposes shall be standard white or better, with a burning test of 43.3° (110° F.) (equivalent to 70° Abel test) or upward, and sp. gr. not below 44° Baumé (sp. gr. 0.804).

The committee appointed by the Baku Section of the Russian Technical Society to examine the new petroleum testing regulations formulated by the government, have reported that sulphuric acid of the prescribed density (1.53) is unsuitable for testing petroleum, the colour of the acid extract being irregular and not sufficiently decisive in gradation. On the other hand, sulphuric acid of 1.73 sp. gr. being found to give concordant results with all grades of petroleum and at all temperatures between 16° and 32°, it is recommended that this strength of acid should be used in the proportion of 40 parts by volume to 100 of oil, the mixture being shaken up in a stoppered glass vessel for 2 minutes, and the acid layer removed and compared with normal solutions of Bismarck brown. The standard solutions are 10 in number, and are graduated so that the highest (No. 1) contains 0.0005% of colouring matter, and the darkest (No. 10) 0.005%, the intermediate shades differing from one another by 0.0005%. The

degree to which the oil has been refined is expressed by the number of
the solution corresponding to the colour of the acid extract, and the
maximum effect in the case of ordinary petroleum distillate is found
to be produced by the use of 0.75% of sulphuric acid (sp. gr. 1.843).
Since few commercial petroleums examined fell below the limits 1 to 8,
the latter shade is recommended as the outside limit for merchantable
petroleum (*J. Soc. Chem. Ind.*, 1896, 678).

Flashing-point.—Cold kerosene oil of good quality will not take
fire when a light is applied, nor will the supernatant vapour inflame.
The temperature at which a sample of petroleum oil commences to
give off sensible quantities of inflammable vapour is technically called
its "flashing-point." Clearly the lower the temperature at which an
oil "flashes," the more dangerous it must be in transportation, storage,
and use. The "flash-point," or temperature of ignition of the vapour,
is greatly reduced by a small admixture of naphtha. Dr. B. W. White
found that when a kerosene oil having a flashing-point of 113° F.
(=45°C) by the open test was mixed with 1% of naphtha, it flashed at
39.4° (103° F.) with 2% at 33.3° (92° F.), with 5 at 28.3° (83°F.), with
10 at 59°, and with 20 at 40° F. On addition of 20% of naphtha, the
oil itself burned at a temperature of 10° (50°F.). The "burning-point,"
"fire-test"—*i. e.*, temperature at which the oil permanently inflames—
is frequently taken as a test of quality, but is not reliable, since oils,
when spilled, will ignite instantly on approach of a flame, when heated
only a degree or 2 above their flashing-point, even although the
burning-point is considerably higher. An oil flashing at 22.7° (73° F.)
by the Abel close test, or at 37.7° (100° F.) by the old open test, will
generally show about 48.8° (120° F.) by the American "fire-test," or
determination of the temperature of permanent ignition. Experiment
shows that an oil flashing at 86° by the open test, and burning at 41.6°
(107° F.), can be made to flash at 37.7° by removing 6 or 7% by dis-
tillation, though such treatment does not improve the oil in other
respects.

Boverton Redwood (*Petroleum and its Products*, Vol. 2) gives a
series of experiments to determine the proportion of air and va-
pours of light petroleums required to produce dangerous explosions.
The apparatus consisted of a glass cylinder or churn, capable of being
rotated at right angles to its longitudinal axis, an arrangement for dis-
placing a known volume of the gaseous contents of the churn by ad-
mission of the required volume of the liquid under examination, and

an explosion chamber. In performing the test, a quantity of the liquid was poured into the churn, which was rotated for a time. After relieving the pressure by permitting a portion of the gaseous contents of the churn to pass into the displacing arrangement, a known volume of the mixture, called air-gas, was driven into the explosion chamber; the contents of this were mixed and a flame applied to a vent.

Petroleum spirit, sp. gr. 0.639, produced a violently explosive mixture when 4% of air-gas was introduced into the explosion chamber. With a spirit of 0.680 sp. gr., the explosion was violent when the percentage of air-gas reached 7.5. With a spirit of 0.700 sp. gr., a violent explosion was produced by a mixture containing 5% of the air-gas. With the vapour obtained from crude American petroleum, over 20% of the air-gas was required for violent explosion.

According to the Petroleum Act of 1871, "the term 'petroleum' includes any rock oil, Rangoon oil, Burmah oil, oil made from petroleum, coal, schist, shale, peat, or other bituminous substance, and any products of petroleum or any of the above-mentioned oils; and the term 'petroleum to which this Act applies' means such of the petroleum so defined as, when tested in manner set forth in Schedule I. to this Act, gives off an inflammable vapour at a temperature of less than 100° of Fahrenheit's thermometer." Petroleum, within the meaning of the Act, is only allowed to be kept and sold under certain restrictions, which vary to a certain extent according to a discretionary power exercised by the local authorities, any breach of the provisions of the Act being punishable by heavy fines.

The Act prescribed a test, known as the open test, by which the flash-point was to be determined. The close test was made compulsory and the open test was abolished by the Act of 1879, but the restrictive legislation prescribed by the Act of 1871 with regard to petroleum with a flash-point under 37.7° (100° F.) was applied to petroleum with a flash-point under 22.7° (73° F.). All petroleum with a flash-point above 73° F. was thus, contrary to the 1871 Act, freed from legislative restrictions. The purpose of a bill now (1899) pending in Parliament is to substitute the accurate or close test for the inaccurate or open test in the Act of 1871, and to restore the 100° flash-point prescribed by that Act.

The open test for determining the flashing- and firing-point was originally performed by heating the oil in a hemispherical porcelain filled to within about half an inch of the brim, the bulb of a thermom-

eter being immersed in the liquid. A lighted taper was passed at
intervals across the oil on a level with the brim of the dish and the
degree noted at which a flash was produced. The fire-test was de-
termined in a similar manner. The method was quite inaccurate,
and not materially improved by the use of Tagliabue's open tester,
which has been adopted as the legal instrument in many localities.
This consists of a small, rather deep glass cup resting in a water-bath,
supported by a metal case and heated by a lamp below; a thermometer
is immersed in the oil which nearly fills the cup, and the testing is
performed as with the older method. The quantity of oil is too small
and the open vessel causes loss of vapour. To obviate this, various
closed testers have been constructed and stirrers have been added so as
to secure the rapid mingling of the oil and consequent thorough heating.
One of the most elaborate of these forms is the Pensky-Martens'
tester. The forms about to be described in some detail are regarded
as satisfactory by many experts and have been extensively employed.

Abel's Closed Oil Tester.—The following abridged description of
the apparatus devised by Sir Frederick Abel is taken from Schedule I
of the Petroleum Act, 1879. It sufficiently indicates the method of
its use.

The test apparatus is to be placed for use in a position where it is
not exposed to currents of air or draughts.

The heating apparatus is filled by pouring water into the funnel
until it begins to flow out at the spout of the vessel. The temperature
of the water at the commencement of the test is to be 54.4° (130° F.)
(neither more nor less).

The test-lamp is prepared for use by fitting it with a piece of flat-
plaited candle-wick, and filling it with colza or rape oil up to the lower
edge of the opening of the spout or wick tube. The lamp is trimmed
so that when lighted it gives a flame of about 0.15 of an in. diameter;
and this size of flame, which is represented by the projecting white
head (F) on the cover of the oil-cup, is readily maintained by simple
manipulation from time to time with a small wire trimmer. When
gas is available, it may be advantageously used instead of the little
oil lamp, and for this purpose a test-flame arrangement for use with
gas may be substituted for the lamp.

The water-bath (B) having been raised to the proper temperature
54.4°, the oil to be tested is introduced into the petroleum cup (A)
(2 in. high by 2.2 in. internal diameter, and made of gun-metal or

brass tinned inside). The oil must be poured in slowly until the level of the liquid just reaches the point of the gauge (c), which is fixed at exactly 1.5 in. from the bottom of the cup. (In pouring in the oil to be tested, great care should be taken not to splash it against the sides of the cup. In warm weather the temperature of the room in which the samples to be tested have been kept should be observed in the first instance, and if it exceeds 18.3°, the samples to be tested should be cooled down to about 15.5°.) The lid (D) of the cup, with the slide closed, is then put on, and the cup is placed in the bath or heating vessel. The thermometer (E) in the lid of the cup has been adjusted so as to have its bulb just immersed in the liquid, and its position, which is adjusted to 1.5 in. below the center of the lid, is not under any circumstances to be altered. When the cup has been placed in the proper position, the scale of the thermometer faces the operator.

The test-lamp is then placed in position upon the lid of the cup, the lead-line or pendulum, which has been fixed in a convenient position in front of the operator, is set in motion, and the rise of the thermometer in the petroleum cup is watched. When the temperature has reached about 18.8°, the operation of testing is to be commenced, the test-flame being applied once for every rise of 1° F. (0.5° C.) in the following manner: The slide is slowly drawn open while a pendulum 24 in. in length performs 3 oscillations, and is closed during the fourth oscillation. (It is obvious that a metronome would be more convenient. Some method of marking time is necessary.) In moving the slide so as to uncover the holes, the oscillating lamp (G) is caught by a pin fixed in the slide and tilted so as to bring the end of the spout just below the surface of the lid. Upon the slide being pushed back so as to cover the holes, the lamp returns to its original position. The temperature at which the vapour of the oil gives a blue flash in applying the test-flame is noted as the flashing point of the sample. To determine the flashing-point of burning oils of very low volatility, the air-chamber which surrounds the lamp is filled with cold water to a depth of 1.5 in., and the heating vessel or water-bath is filled as usual, but with cold water instead of water at 54.4°; the heating lamp under the apparatus, and kept there during the entire operation. If a very heavy oil is being tested, the operation may be begun with the water heated to 48.8°.

The results of this method are satisfactory. The flashing of the

vapour occurs at a temperature much lower than was the case with the old apparatus for the open test.

The flashing-point of a sample of kerosene, as determined by Abel's apparatus, has been found to be sensibly lower in India and the tropics than when the same oil is tested in temperate climates. A sample which, under ordinary circumstances, flashed at 22.7°, had a flash-point of 18.8° when examined in a tropical region. The difference is due to the fact that at a high atmospheric temperature the more volatile hydrocarbons are less readily held in solution in the oil, and the least agitation, such as is involved in pouring the oil into the cup, determines their vapourisation. To obtain concordant results in hot countries Abel and Redwood recommend that the operator should commence to apply the test-flame at a much lower temperature (13.3) than that prescribed in the Act, which is when the oil in the cup has acquired a temperature of 18.8°. This modification causes the removal of the superincumbent vapours in quantities too small to flash, by currents of air set up by each application of the gas flame. Even with this modification of the test, a sample which flashes at 22.7° in England will flash at about 21.1° in India. It is evident that the causes which lead to errors in India will have a tendency to affect the test in temperate countries, and to render the flash-point of the same oil lower in summer than in winter, but this tendency can be counteracted by bringing the sample to be tested to 13.3° before commencing the operation. Changes in barometric pressure also affect the flash-point of kerosene, a fall of 1 in. of the mercury in the barometer lowering the flash-point of an oil by about 1°.

S. Gray (*J. Soc. Chem. Ind.*,, 1891, 348) has described a stirrer attachment to the Abel cup, by which it is claimed that the results are more correct, are independent of its manner and rate of heating. The apparatus consists of 2 sets of vanes—one in the oil and the other in the vapour-space—with beveled gearing, or arranged that it may be easily put in or out of gear and the lighting attachment brought into action. There are 3 orifices—one central for the test-light, the others for admission of air. The change from stirring to testing, and *vice versa*, can be made promptly. The Pensky modification is also the introduction of a stirrer. Martens has still farther improved the apparatus.

New York State Closed Oil-tester (*Elliott Tester.*)—As a result

of investigations, Elliott devised a form of tester which has been highly approved. It consists of a copper cup holding about 300 c.c. immersed in water, which can be heated by a small flame. The cup is covered by a convex clock-glass, which is perforated in the centre to permit the passage of a thermometer, and has a notch at the edge for insertion of the testing flame. The official directions are: Fill the water-bath with cold water up to the mark, place the oil-cup in it, and pour in enough oil to fill the cup up to the flange that joins the cup with the vapour-chamber above. The oil must not flow over the flange. Air-bubbles may be removed by means of dry paper. The glass cover is then put on, and the thermometer placed so that its bulb is just covered by the oil. A small flame must be used for heating, so that the rise in temperature should be about 2° per minute, never over 3°. For the igniting flame a gas jet 0.25 in. in length is employed. When gas is not at hand, a piece of waxed linen twine may be used. The flame should be small. Testing should begin when the oil reaches the temperature of 29.3° (85° F.). The torch is inserted through the testing notch at such an angle as to well avoid contact with the glass, and to a distance about midway between the surface of the oil and the under surface of the cover. Its movement must be steady, uniform, swift, and without pause, and should be repeated at every 1° C. or 2° F.; increase until the thermometer marks 35° (95° F.), when the heating flame should be shut off and the testing made at each 0.5° C. or 1° F. until 37.5° C. or 100° F. is reached. After this the heating flame may be again started, if necessary, and the testing continued for each 1° C. or 2° F. as at first. The appearance of a slight bluish flame indicates that the flashing-point has been reached. In every case the temperature of the oil should be noted *before* the testing flame is introduced. This flame must not touch the oil. The water-bath must be refilled with cold water, and the oil cup well cleaned for each test. This tester is largely used in many laboratories and designated in many official specifications, particularly in the States of Georgia, New Jersey, New York, and South Dakota. *The Foster automatic tester* is used in several States of the United States and deserves mention. The instrument consists in a copper stand with water-bath and oil cup, which latter is covered; the thermometer and flashing taper arranged at the foci of an ellipse, which is the shape of the cup. When flashes are made air passes down a space surrounding the thermometer, and probably because of this ventillation this tester gives results

according to Redwood from 14 to 20° F. higher than those obtained by using the abel instrument. The use of this tester is prescribed by law in Kansas, Michigan, Nebraska, North Dakota, Ohio, and Washington, U. S. A. Engler's tester, which is used in Germany, employs an electric spark from a small induction coil to fire the petroleum vapour in a chamber which has 2 metal shutters, which are lifted by an explosion as soon as the atmosphere through which the spark is passing becomes sufficiently charged with vapour.

The following allowances in flash and fire tests are made for variations in the barometric pressure in excess of, or less than, 7.60 mm.

765 mm. add 0.2°	755 mm. deduct 0.2°
770 mm. add 0.4°	750 mm. deduct 0.3°
775 mm. add 0.5°	745 mm. deduct 0.5°
780 mm. add 0.7°	740 mm. deduct 0.7°
785 mm. add 0.9°	735 mm. deduct 0.9°
790 mm. add 1.0°	730 mm. deduct 1.0°

FLASH AND FIRE TESTS REQUIRED IN DIFFERENT COUNTRIES AND INSTRUMENTS PRESCRIBED.

Country	Instrument	Flash	Fire	When act passed
Great Britain	Abel...............	73° F.	....	1879
Canada...............	Abel...............	85° F.	....	1899
France...............	Granier.............	....	35°	1873
Germany, Bremen...	Abel...............	21°	....	1872
Germany, Berlin.....	Abel-Pensky.........	21°	....	1883
Germany, Hamburg	Abel-Pensky.........	21°	....	1882
India................	Abel-Pensky.........	70° F.	....	1899
Japan................	(Closed test)........	86° F.	....	1882
Russia...............	Abel-Pensky.........	28°	....	1891
Sweden..............	Abel...............	22°	(71.6° F.)	1885

In Germany and in Russia the Abel-Pensky apparatus is prescribed. When the oil flashes below 60°, the oil cup is to be inserted direct into the water-bath, the temperature of the latter being about as high again as the expected flashing-point, so that when this is beyond 50°, the water must be boiling. For oils flashing between 60° and 85° the space between the oil cup and the water-bath must be filled with a heavy mineral oil (sp. gr. over 0.900), and the water maintained at about 15° above the flashing-point anticipated. A preliminary test having been made, the test-flame is first applied and the temperature is 5° below the flashing-point thereby ascertained. Only when the oil

flashes between 27° and 29° is a correction for atmospheric pressure to be made. For all heavy burning and lubricating oils and residuum flashing above 85°, the Pensky-Martens instrument is necessary.

The tests required in the different states of the United States, where the regulations are enforced, are as follows:

States	Instrument	Flash °F.	Fire °F.
Arkansas.................	Tagliabue cup.........	....	130°
California (San Francisco).	Tagliabue cup.........	100°	....
Colorado (Denver)........	Tagliabue cup.........	110°	....
Connecticut.............	Tagliabue cup.........	....	110°
Delaware.................	Tagliabue cup.........	....	150°
Georgia..................	Elliott................	100°	....
Idaho....................	Tagliabue cup.........	....	120°
Illinois.................	Tagliabue cup.........	....	150°
Indiana..................	Tagliabue cup.........	120°	....
Iowa.....................	Elliott................	105°	....
Kansas...................	Foster..............	110°	....
Kentucky.................	Tagliabue...........	....	130°
Louisiana...............	Tagliabue...........	125°	....
Maine...................	Tagliabue...........	....	120°
Maryland (Baltimore).....	....	....	120°
Massachusetts...........	Tagliabue open cup....	100°	....
Michigan................	Foster................	120°	....
Minnesota...............	Minnesota cup.........	....	120°
Nebraska................	Foster................	112°	....
New Hampshire...........	Tagliabue cup.........	110° or 120°	....
New Jersey..............	Elliott cup...........	100°	....
New Mexico..............	Tagliabue cup.........	....	120°
New York................	Elliott................	100°	....
North Dakota...........	Foster................	100°	....
Ohio....................	Foster................	120°	....
Oklahoma................	Tagliabue cup.........	120°	....
Oregon..................	....	....	120°
Pennsylvania............	Tagliabue open cup....	....	110°....
Rhode Island...........	Tagliabue cup.........	110°	....
South Dakota...........	Elliott cup...........	105°	....
Tennessee..............	Tagliabue............	120°	....
Utah...................	Tagliabue cup.........	110°	....
Vermont................	Tagliabue cup.........	....	110°
Virginia (Richmond)......	Tagliabue cup.........	....	110°
Washington.............	Fester cup............	120°	....
Wisconsin..............	Tagliabue.............	....	120°
Wyoming................	Tagliabue.............	....	120°
Missouri...............	Tagliabue cup.........	....	150°
Montana................	Tagliabue cup (?).....	110°	....

Fractional distillation is carried out the same for kerosene as for crude oil (page 48).—Mineral burning oils should not give a high percentage below 150°, and, on the other hand, should not have a

large proportion of "tailings" or heavy oil, distilling above 300°. By judicious manipulation of a mixture of naphtha and heavy oil, kerosene may be sophisticated without altering the sp. gr. and without reducing the flash-point so as to excite suspicion. Such an oil will not be satisfactory, as the more volatile portions will be consumed first, the heavy viscous portions remaining to clog the wick.

J. Biel recommends that the fractional distillation of mineral burning oils should be conducted on 250 grm. of the sample, in a glass flask of 500 c.c. capacity. This is wrapped round tightly with thin brass gauze or glass wool, to protect it from too rapid changes of temperature and is connected by a Glynsky's dephlegmator (Vol. 1, page 21) with a Liebig's condenser. The thermometer is fixed in the dephlegmator so that the bulb may be on a level with the exit-tube. At the commencement, the flame under the flask should not be larger than is requisite to drive over the light oils, which are collected as long as any notable quantity (more than 10 drops per minute) of oil distils at 150°. The flame is then enlarged, and the "normal petroleum" distilling between 150° and 270° is next driven over, the receiver being changed when no appreciable quantity distils when the thermometer is maintained at the latter temperature. Biel weighs the distillates, and ascertains the amount of the residue or "tailings" by noting the difference between the weight of the flask and dephlegmator on the completion of the distillation and again after cleaning. It is evident that the method of measurement commonly employed in practical examinations of volatile oil is equally available.

The following results obtained by Biel by the foregoing process are interesting as showing the behaviour of typical samples of Russian oils:

	Kerosene			Pyronaphtha	
	A	B	C	D	E
Sp. gr.	0.820	0.820	0.835	0.857	0.867
Flash-point,°	52.5	35.0	44.5	7.5	94.0
			Percentage		
Light oils (below 150°)	0.8	10.0	6.0	0.0	0.0
Normal oils (150° to 270°)	92.0	76.5	63.5	44.5	30.5
Heavy oils (tailings)	7.2	13.5	30.5	55.5	69.5

Beilstein[1] states that the rule for Russian petroleum is that an oil to be considered safe should yield less than 5% of "light oils," and less than 15% of "heavy oils." With American petroleum, the "heavy oils" should not exceed 15%. (See also description of Regnault's apparatus, under "Benzin.")

As already stated, Russian kerosene is usually of distinctly higher density than that from American petroleum. Russian petroleum gives much the smaller yield of burning oil, but the product is more nearly homogeneous, the hydrocarbons composing it not differing widely in sp. gr., b. p., and other characteristics. This peculiarity is well shown by the following figures obtained by B. Redwood by fractionally distilling samples of kerosene made from Baku and American petroleum. A measured quantity of the liquid was distilled, and the density of each fraction of 10% was observed:

Kerosene	Russian kerosene, sp. gr. 0.822	American kerosene, sp. gr. 0.803
First fraction.....................	0.783	0.748
Second fraction..................	0.796	0.759
Third fraction...................	0.803	0.778
Fourth fraction..................	0.814	0.792
Fifth fraction...................	0.827	0.802
Sixth fraction...................	0.831	0.812
Seventh fraction.................	0.837	0.822
Eighth fraction..................	0.838	0.831
Ninth fraction...................	0.846	0.838
Tenth fraction (residue).........	0.864	0.849

In Russian kerosene there is less difference between the sp. gr. of the lightest and heaviest fractions than in American oil.

The **sp. gr.** is almost universally determined by means of hydrometers and the readings made in either degrees Baumé or sp. gr. The sp. gr. bottle and the Westphal balance are also used. (See appendix for Conversion Table of sp. gr. to degrees Baumé.)

D. Mendelejeff has determined the corrections to be applied for the differences of temperature above or below the standard temperatures of 60° F. (in America and Great Britain) and 15° C. (on the Continent).

[1] *Zeit. Anal. Chem.*, 1883, 14.

Sp. gr.	Correction for each degree, C.
0.760 to 0.780	0.000790
0.780 to 0.800	0.000780
0.800 to 0.810	0.000770
0.810 to 0.820	0.000760
0.820 to 0.830	0.000750
0.830 to 0.840	0.000740
0.840 to 0.850	0.000720
0.850 to 0.860	0.000710

Before using a hydrometer it is well to compare it at several points on the scale with a sp. gr. bottle of known capacity.

The Westphal balance is sometimes used for the determination of the sp. gr.

A test of kerosenes by burning them in similar lamps and noting the rates of consumption and the comparative intensities of the light yielded, is often capable of giving valuable information. Much depends on the character of the wick used, all oils burning far more satisfactorily and safely with an American wick of long staple cotton loosely woven, than with the comparatively hard, tightly-woven wick often employed in Great Britain. Kerosenes containing a large proportion of light oils give a better light, but burn faster than others, while the presence of heavy oils retards the consumption and seriously diminishes the light yielded. Care must be taken not to form too hasty an opinion on the oils tested, as a kerosene containing excess of both light and heavy oils, or in technical phrase consisting largely of "mixed tops and bottoms," may give a good light at first, but after some time the flame will greatly diminish in size and luminosity, and in extreme cases the wick becomes so clogged and charred as to cause extinction. Russian kerosene does not give so much light as American, but, on the other hand, there is considerably less diminution as the level of the oil falls in the reservoir.

Odour.—This is a matter that depends upon the experience of the analyst. Odours indicative of imperfect refining, etc., would class the oil unmerchantable.

The colour of kerosene is determined by means of specially constructed forms of apparatus for accurately gauging the colour. Two forms may be mentioned here which are used both in England and Germany, the Wilson chromometer and the Stammer chromometer.

The Wilson tester compares a column of oil 16 in. long with a colour reflected from a glass disc. The discs indicate 4 commercial grades: 1. Water-white; 2. Superfine white; 3. Prime white; 4. Standard white. This tester does not define the colour sufficiently for particular work, and on that account the tester about to be described is to be preferred.

The Stammer Chromometer.—To meet this want, the Stammer chromometer was introduced, in which the length of the oil column can be varied, so that by starting with a standard of paler tint of the sample, the column of oil may be shortened until the two match, and the colour of the oil may thus be found in terms of the standard, 40 on the scale of Stammer's chromometer being equal to standard white, 50 to prime white, and 190 to superfine white.

Stammer's chromometer is now made in an improved form without the wooden case.

The use of the single-glass standard provided with this instrument was found by Redwood to be open to serious objection, as the variations in colour of different samples necessitated the shortening of the column of oil so much in certain cases that the sensitiveness of the test became greatly impaired. Several important modifications introduced by Mr. Robert Redwood have, however, overcome this defect, and by means of the improved instrument employed in Redwood's laboratory, it is easy to record accurately the colour of any sample on a scale ranging from "water-white" (1) to standard white (4). The space between any 2 of the 4 shades is divided into 10 equal parts, so that if the colour, for instance, of a sample is midway between "water-white" and "superfine white" it would be indicated by the number 1.5.

Another method of procedure that has been used in testing the colour and may be useful where chromometers are not available and for standardising purposes:

The colour of the normal glass marked Sn. W. (standard white) corresponds exactly to the colour of a solution of 0.00095% K_2CrO_4 acidified with 5% sulphuric acid of a height of a column of solution of 404.6 mm. See Table I from Rakusin. Lovibond's[1] tintometer is an elaborate instrument adapted for analysis of, measuring, and recording of colours.

The following grades of colour are recognised in the trade: 1. Water-white. 2. Superfine white. 3. Prime white. 4. Standard white.

[1] Now much used in England.

The following table shows the relations between the markings of the Wilson chromometer and the Stammer modification:

```
Standard white 4.. ...............................  50   mm.
Standard white 3 1/2 ...........................  68   mm.
Prime white 3.................................  86.5 mm.
Prime white 2 3/4 .............................115   mm.
Prime white 2 1/2 ............................143   mm.
Prime white 2 1/4 ............................172   mm.
Superfine white 2 .............................199   mm.
Superfine white 1 1/2 .........................255   mm.
Water-white 1.................................310   mm.
```

In some cases a diminution of light may be due to the presence of mineral ingredients; *i. e.*, compounds of calcium or magnesium. These may be detected by reducing a moderate amount of the oil to ash, dissolving the residue in hydrochloric acid, and applying the usual precipitation tests.

The following methods of determining burning value are taken from Redwood:

Burning Quality Test.—Although the distillation test affords an indication of the value of an oil for illuminating purposes, more practical results are obtained by burning the oil in lamps under conditions as close as possible to those existing in ordinary use.

In most of the United States refineries the oil is tested by burning it in lamps of ordinary construction, and noting the diminution in the size of the flame after a certain time. The results thus obtained depend upon many variable conditions, and attempts have been made to eliminate some of the sources of variation.

Saybolt's Apparatus.—The Saybolt testing-lamp consists of a tall graduated glass vessel with a burner which gives a flame of considerable height in comparison with its width. The chimney is also graduated so that the height of the flame may be measured. A carefully selected wick is used, and the lamp is burned with the reservoir in a vessel of water at 60° F. The depression of the oil-level and the diminution in the height of the flame at the expiration of a given time are noted, and the "burning quality of the oil is judged therefrom."

Canadian Method.—In Canada the "burning percentage" was formerly determined by the use of a lamp thus described: "The bowl of the lamp is cylindrical, 4 in. in diameter and 2.75 in. deep, with a neck placed thereon of such a height that the top of the wick tube is

3 in. above the bowl. A 'sun-hinge' burner is used, taking a wick
0.875 in. thick and a chimney about 8 in. long." The test is conducted
as follows: "The lamp bowl is filled with the oil and weighed, then
lighted and burned up full flame, just below the smoking-point, and
burned without interference til 12 ounces of the oil are consumed. The
quantity consumed during the first hour and the last hour is noted."
The ratio of the 2 quantities is then measured of the burning quality,
and the percentage the latter quantity is of the former is the burning
percentage referred to.

Redwood's Apparatus.—In Redwood's laboratory, the wicks
employed in ascertaining the burning quality of oils are examined
by means of special apparatus, and any defective portion is rejected.
The test consists in arranging a given length of the wick so
as to draw, by capillarity, a mineral oil of known quality from a
vessel, at a fixed temperature, the value of the wick being gauged
by the amount of oil drawn out in a certain time. The wick is
dried immediately before use, and immersed in the oil while warm.
The oil chambers of the lamp in which the tested wicks are subse-
quently used are of uniform dimensions, and the burners are first
tested to ascertain that they give similar flames with the same oil.
The wick should be very carefully trimmed, and the oil in the lamp
should be kept at a constant temperature, preferably at 60° F. The
wick should be raised to yield the largest flame obtainable without
smoke. For registering variations in the size and shape of the flame
during the test, a camera is employed by Redwood, by means of which
the outline of the flame may be traced at intervals on thin paper.
No general agreement has, however, been arrived at as to the extent
of diminution allowable in the flame from an oil classed as of satis-
factory burning quality. The apparatus already described is also
employed by Redwood in determining the relative capillary values of
various oils.

Illuminating Power.—The following table gives the results of
comparative photometric tests made by Redwood with American
kerosene and Russian kerosene (Nobel's make), in ordinary lamps
with Hinks's duplex burner[1] and the 2 kinds of wick, some loosely
woven, and the other somewhat more tightly woven:

[1] These tests were not made with the present form of his burner, which has a higher
illuminating power for a given consumption of oil.

BITUMENS.

PHOTOMETRIC COMPARISON OF KEROSENES.

	American kerosene		Russian kerosene	
	Loosely woven wick	Tightly woven wick	Loosely woven wick	Tightly woven wick
	Standard candles	Standard candles	Standard candles	Standard candles
Maximum illuminating power.........	25.59	24.25	22.1	19.14
Maximum illuminating power, after six hours.	22.24	19.16	20.5	17.4
Average illuminating power, during six hours,	23.96	22.14	21.2	18.04
Diminution in illuminating power in six hours.	13.0	20.9	7.2	9.0
	Grains	Grains	Grains	Grains
Oil consumed per hour...............	1238	1213	1137	981.6
Oil consumed per candle-light per hour.	51.6	54.7	53.6	54.4

The Russian oil did not give as much light as the American, but there was much less diminution in the illuminating power as the level of the oil in the reservoir became depressed.

Sulphur compounds exercise an injurious effect upon the illuminating power of kerosene. Specimens containing large proportions of olefines, as do those obtained by cracking, are apt to contain sulphonates. These may be detected by a method given in connection with the examination of lubricating oils. For the detection of ordinary sulphur compounds the oil should be heated to boiling for some time with a fragment of sodium, in a flask furnished with an inverted condenser. After cooling, water is added drop by drop to the contents of the flask till the sodium is oxidised. More water is then added; the aqueous liquid separated, and the solution tested with a drop of sodium nitroprusside, which will produce a fine violet-blue colouration if the sample contained sulphur. Sulphur can be estimated by burning a known weight of the oil in a standard gas-testing apparatus and precipitating the acid condensed with the water, as barium sulphate. The Carius and Sadtler crucible methods are not very suitable. Sulphur is a highly objectionable ingredient, owing to the formation of corrosive and poisonous bodies when the oil is burned.

Sulphur is best estimated in kerosene by burning a weighed amount in a lamp and passing the products of combustion through a solution which oxidised the sulphur gases to sulphuric acid so that the sulphur can be determined as barium sulphate. Allen's modification of the methods of Heussler and Engler which carried out this procedure

is as follows: The oil is burned in a small lamp, air is drawn into a small chamber surrounding the lamp, and the products of combustion are drawn through the absorbing vessel by means of suction. The solution used for absorption is solution of bromine in a 5% solution of potassium hydrate or carbonate. The methods of Kissling, Ohlmüller, etc., differ chiefly in having other absorbing solutions, but S. Friedländer compared the different ones and found them to give practically identical results. The reviser of this section has been told that water alone can be used and the sulphuric acid coming over can be titrated with standard alkali. The flow of SO_3 must certainly be very slow, however, as it is a well-known fact that SO_3 is not taken up to any extent by water, it being necessary in manufacturing practice to use only slightly diluted sulphuric acid to absorb SO_3.

An annoying turbidity sometimes develops in refined oil. It has been ascribed to various causes, such as the size used on the inside of the casks, but, according to Vieth (*Ding. Poly. Jour.*, **277**, 571), the usual cause is the failure to remove all the sulphonic acids formed during the treatment of the oil with sulphuric acid in the refining process. The turbidity often appears in the dark and disappears when the sample is exposed to light and air. The only means of preventing it appears to be by treating the fresh distillate with about 1% of sodium hydroxide solution of 1.3 sp. gr., separating the solution, treating the oil with sulphuric acid, washing thoroughly, again treating with sodium hydroxide, and repeating the process until the oil is no longer affected by the alkali. All the alkali must be washed out before the oil is marketed.

Optical Activity.—This optical activity of petroleum and petroleum distillates has become a very important subject in recent years because of its bearing on the origin of petroleum. It is not now, nor is it likely to become, an important matter analytically, as the total amount of rotation is so slight; and if much coloured, crudes and even distillates have to be so much diluted with an inactive solvent, such as benzene, that the small optical rotation that might have been observed is not distinguishable.

A. Rakusin recommends the use of the Ventzke (sugar) scale and white light. If the polariscope (with sodium light) is used the following relation is used in the calculation:

100° Ventzke = 34.68° on the circular scale.

If an oil is too dark in colour it can either be diluted, as above referred to, or read in a shorter tube. Instead of a 200 mm. tube, a 100 mm. or even a 50 mm. may be used.

For distinguishing between the products of Russian and American petroleum, and for detecting admixtures of crude with refined oil, Riche and Halphen[1] have devised a test depending on the proportion of a special solvent required to form a clear solution with a definite weight of the sample. The solvent is a mixture of equal parts of anhydrous chloroform and 93% alcohol. The quantity of oil taken is 4 grm. in each case. Reference must be made to the original paper for the tables showing the comparative results with mixtures of known composition. Redwood states that the method is satisfactory if the strength of the alcohol be rigidly adhered to.

GAS OIL.

The oils used for gas-making are usually those yielding only small percentages of kerosene and are distilled for gas oil to the exclusion of nearly all other products. There may be some benzin caught and some heavy lubricating oils before coking stage is reached, but the main product is the single cut of gas oil. Texas oil is much used for this purpose as are many other crudes, but particularly those that do not yield good kerosene fractions. These oils may be sold on their sp. gr. distillation record and sulphur contents or on their actual gas-making value.

Owing to the rapid increase in the number of works using oil as an important element in gas-making, the matter of the selection of a suitable gas oil has become a matter of importance and tests have had to be devised for the purpose.

The chief test to be applied is that of using a small retort to determine the amount of gas obtainable and its candle-power as well as the yield of tar. J. F. Tocher (*J. Soc. Chem. Ind.*, **13,** 231 (1894)) described a cylindrical iron retort 36 by 6 in., and in a series of tables showed the nature of the products (1) from various oils; (2) from various hydrocarbons, and (3) the character of mixtures of oil-gas and coal-gas in various proportions. Although there have been better constructed retorts introduced for laboratory tests more recently, the results of Tocher are of considerable value.

[1](*Jour. Pharm. et Chim.*, **30** (1894)),

TABLE I.—PRODUCTS YIELDED BY VARIOUS OILS.

Temperature	Mineral naphtha sp. gr. 0.730		Burning oil sp. gr. 0.807		Mineral oil sp. gr. 0.847			Mineral oil sp. gr. 0.884		
	600°	850°	600°	850°	600°	800°	1100°	500°	600°	850°
Cubic feet per gallon of oil.	72	100	75	93	64	82	95	34	59	108
Colour of gas..........	White	White	White	Brownish-white	White	Light brown	Dark brown	Light yellow	Light yellow	Brown
Composition of gas	%	%	%	%	%	%	%	%	%	%
C_nH_m hydrocarbons	31.2	29.8	32.8	43.1	33.7	46.2	21.5	44.7	40.5	35.7
C_nH_{2m+2} hydrocarbons	47.6	48.7	57.0	47.2	50.1	39.4	49.2	40.1	48.2	46.3
Hydrogen...............	17.4	19.1	7.1	7.6	13.7	11.9	28.4	12.7	8.1	16.1
Carbon density of C_nH_m ..	2.67	2.71	3.93	2.92	2.88	2.75	2.41	3.11	2.95	2.79
Hydrogen density..........	....	....	....	....	4.87	5.22	5.16	5.38	5.54	4.46
Illuminating power In candles corrected to 5 cu. ft. of gas and 120 grains sperm per hour	43.5	42.2	48.7	61.4	52.5	64.8	36.2	63.8	57.7	49.0
Candles per gallon........	626	844	730	1142	672	1062	688	434	681	1058
Pounds sperm per candle.	3292	4437	3482	5447	3046	4815	3119	1885	2958	4596
Enriching value, pounds sperm	....	....	....	6% mixture gave 10,174 enrichment figure= 118.	....	5% mixture gave 6,872; enrichment figure= 96.5	....	....	....	....
% residuals.............	11.4	5.1	21.4	7.5	28.5	12.2	18	62.3	41.5	9.4

TABLE II.— PRODUCTS YIELDED BY VARIOUS HYDROCARBONS.

Temperature	Octane, C_8H_{18}; b.p. 122°		Decane, $C_{10}H_{22}$; b.p. 156.5°		Turpentine oil, $C_{10}H_{16}$; b.p. 154°–158°	Naphtha, 0.730	Mineral oil, 0.884	
	550°	800°	550°	800°	800°	850°	500°	850°
Yield.........	18 litres per 100 c.c.	42 litres per 100 c.c.	24.6 litres per 100 c.c.	47.5 litres per 100 c.c.	63.3 cubic feet per gal.	100 cubic feet per gal.	34 cubic feet per gal.	0.108 cubic feet per gal.
Colour of gas.........	White	White	White	White	White	White	Light yellow	Brown
Composition of gas.								
C_nH_m hydrocarbons.........	23.5	12.3	27.4	13.4	19.1	29.8	44.7	35.7
C_nH_{2m+2} hydrocarbons......	39.4	35.4	36.0	50.1	54.1	48.7	40.1	46.3
Hydrogen.........	35.7	52.8	35.7	36.5	26.8	19.1	12.7	16.1
Ethylene equivalent of C_nH_m..	30.0	11.7	32.1	14.2	30.4	35.2	69.5	49.8
Carbon density.........	2.56	1.91	2.35	2.12	3.20	2.71	3.11	2.79
Illuminating power in candles per 5 cubic feet.	18.0	....	20.2	12.0	39.1	42.2	63.8	49.0
Residuals, %.........	22.0	a few drops	50.0 Composed almost entirely of unchanged decane	none	16.6	5.1	62.3	9.4

The most practical laboratory retort for determining the gas value of an oil that has been devised is that of Helfers (*Z., Angew. Chemie*, 1896, 451). Fig. 5 shows the retort and connections. 100 c.c. of oil is
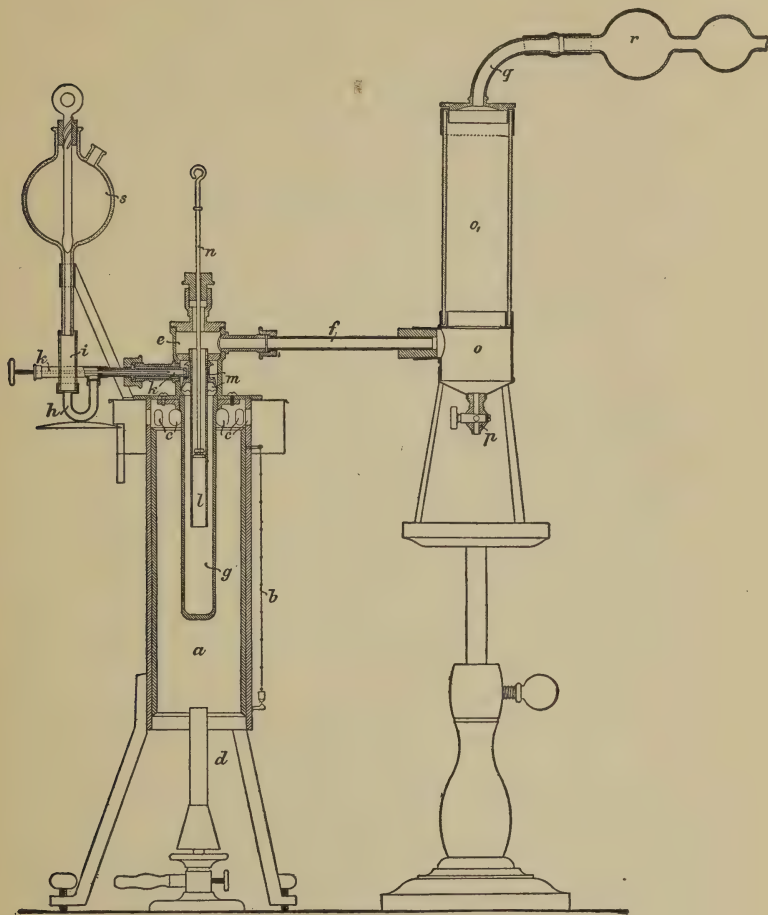
FIG. 5.

placed in the Hofmann funnel *s* and goes through the glass cylinder *i* and the U-tube *h* to the needle valve *k*, where it is admitted a drop at a time into the retort *g*. The passages *s*, *h* and *k* are weighed before and after the test to get the exact weight of oil taken and the retort *g* for

the amount of coke and o o for tar. The oil is introduced at the rate of 10–30 drops per minute after the retort has been brought up to red heat. If the delivery tube becomes clogged with tar the piston n is used to force a passage. When the gas-making is normal the gas has a brown colour and the tar is dark coloured; if the gas is white and the tar clear brown there has been an incomplete gassification.

The candle-power of the gas on an average gas yield of 50 cubic meters from 100 Kg. of oil is calculated according to the following formula:

A = gas yield, C = amount of coke, T = the amount of tar and L = photometric value of the gas. $L_{50} = L \dfrac{(A-50)\ (C\ T)}{100}$ in regular gas ovens.

The conditions of an experiment carried out by F. Frank (Holde, Untersuch d. Mineralöle u. Fette, f. 64) were as follows:

Temperature of the upper retort {	limits.........	670–690°
	average.......	680°
Temperature of the lower retort {	limits.........	740–750°
	average.......	745°
Time of experiment...........................		40 minutes
Amount of oil gassified......................		12.91 kg.
Resulting gas in cubic metres.................		7.70 m3.
Resulting tar		4.45 grm.
Gas oil used for one run....................		19.37 kg.
Gas yield for one run.......................		11.55 m3.
From 100 kg. of oil there was obtained:		
Gas in m3............................		59.64
Gas in kg............................		34.47
The gas burning at the rate of 35 litres per hour in burner No. 60 gave the following in Hefner candles		11.3

CALORIFIC VALUE.

Sherman and Kropff (*J. Amer. Chem. Soc.*, **30**, 1626–31 (1908)) found that fairly exact relations existed between the sp. gr. of petroleum oils and their calorific power. 64 samples of typical American petroleum oils, from the chief oil fields and ranging from light gasolene to heavy crude oil were examined. The relationship is expressed in British thermal units per pound, and compared with the density, expressed in degrees Baumé. The following formula expresses the relationship approximately.

B. T. U. = 18,650 + 40 (Baumé degrees − 10).

In the case of nearly 90% of the samples examined the difference between the observed and calculated calorific powers was less than 1%; it was greater than 2% in 1/30 of the cases, and in no case was greater than 3%.

A sp. gr. of 0.7–0.75 indicates about 11,700–11,350
A sp. gr. of 0.75–0.8 indicates about 11,350–11,100
A sp. gr. of 0.8 –0.85 indicates about 11,100–10,875
A sp. gr. of 0.85–0.9 indicates about 10,875–10,675
A sp. gr. of 0.9 –0.95 indicates about 10,675–10,500

Only 2 of 63 samples showed a difference of as much as 100 cals., and 7 of as much as 50 cals. between the observed and calculated powers.

KEROSENE EMULSIONS.

So-called kerosene emulsion used for spraying fruit trees, etc., are mixtures of soap, kerosene and a little water. In addition to kerosene there may be tar acids combined as soaps and aromatic hydrocarbons. Crude petroleum may be used instead of kerosene.

The emulsion may be broken and the oil extracted by drying, but that means loss of light constituents of the oil. The best way probably is to add enough alcohol to a measured portion for analysis to completely break the emulsion and then add two or three times as much ether as alcohol and proceed as given on page 169. The "Reviser" suggested this method quite recently (*J. Ind., and Eng. Chem.*, 1909, **1**, 479).

The soaps generally contain rosin as well as fatty constituents. The soaps from these mixtures are examined after the removal of the oils, as just referred to, and any separation of different kinds of oils is effected after driving off the ether. Benzene homologues can be separated from petroleum oils by means of conc. nitric acid which converts the former into nitro-derivatives.

Water is estimated in kerosene emulsion by means of distillation from a retort. The "Reviser" used a cylindrical copper retort holding about 1 litre, obtained from the Barrett Manufacturing Co., of Philadelphia. The burner is ring-shaped and surrounds the retort. With many oils water causes frothing, so it has been found best to start the heating with the burner at about the upper level of the liquid and then lower it after danger of frothing is over. A little petroleum ben-

zin (62° B.) may be added in cases where the hydrocarbons are of high b. p. so as to carry over the water.

Soaps are estimated in mineral oil by drying to remove water and then thinning out with petroleum or sulphuric ether, and filtering off the insoluble soap. This method is applicable for alkali soaps, lime, or alumina soaps. The bases can be estimated by burning off the oil and decomposing the soaps, leaving the alkali and lime as carbonates and alumina as oxide. The alkalies can be titrated with methyl orange as an indicator. (See lubricating greases, page 177).

LUBRICATING OILS.

Lubrication has for its object the reduction of friction between moving surfaces. In the sliding friction of solids the magnitude of the resistance is, up to the point of abrasion, dependent on the character of the surfaces, and proportional to the force with which they are pressed together, though when the pressure is very low, the resistance may be principally due to the adhesion, in the case of lubricated surfaces. In fluid friction, on the other hand, the resistance is proportional to the area and velocity of the surface exhibiting it, and to the density and viscosity of the liquid. In the practical application of lubricants to the rubbing surfaces of machinery in motion, the friction is usually compounded of the friction of solids and of fluids in proportions varying in each case. In cases, however, in which it is practicable to float the moving part in the lubricant, fluid friction alone is concerned; while in the case of slowly moving heavy machinery, the resistance is chiefly due to the friction of solids.

In theoretically perfect lubrication the resistance would be independent of the pressure. The more viscous the lubricant, the greater the pressure which can be sustained without squeezing out the film of lubricant from between the moving surfaces; but *unnecessarily* high viscosity creates unnecessary fluid friction, and the viscosity of the lubricant should therefore be proportional to the pressure. In other words, the lubricant should have just sufficient "body" or viscosity to keep the moving surfaces apart, under the maximum pressure. Hence for heavy machinery a highly viscous or even solid lubricant must be employed, and oils are not unfrequently wholly or partially replaced by graphite, steatite, wood saturated with waxes, etc. (so-called oilless bearings). In some cases the viscosity of the oil is increased by an

admixture of soap or by adding alkali. The following table shows the composition of 3 mixtures used for lubricating the axles of railway carriages:

	English		German
	Summer	Winter	
Tallow..............................	504	420	246
Palm oil..............................	280	280	98
Rape oil..............................	....	....	11
Sperm oil..............................	22	35	....
Caustic soda..........................	120	126	52
Water................................	1370	1524	593

Rosin grease is a mixture of similar consistency, largely employed for lubricating the wheels of carts and colliery trucks.

A combination recently introduced is Acheson's "oil-dag" or lubricating oil in which is suspended deflocculated graphite, or graphite which has been brought to a very finely divided state by a process invented by E. G. Acheson, of Niagara Falls, N. Y. For delicate movements, such as exist in clocks and watches and light and fast-running machinery, the thinnest oils are suitable.

A thick oil takes a greater power to drive, and develops a higher temperature than an oil of low viscosity; and, as a rule, the lubricant should be as thin as is consistent with the weight of the machinery and the temperature to which the oil will be subjected. With ample driving power a moderately thick oil may be used for heavy machinery, particularly if the temperature be high, but if the driving power be inadequate, it may be necessary to use a thinner oil.

Although the foregoing is the main principle governing the choice of lubricants, the degree of viscosity required is also dependent on the fit of the bearing surfaces and upon the character of the motion, and these conditions vary largely in each case. It is very difficult to predict the behaviour of a particular oil in practice from its trial in a mechanical testing machine. On this account, as also from the more efficient of them necessitating the use of steam-power, the ingenious machines devised for testing lubricating oils have not fully justified the anticipations of their inventors. The only rational plan of applying such tests is to use a series of standard spindles for testing

spindle oils, standard bearings for axle-lubricants, and so on for other oils. This requirement is practically prohibitory of the use of mechanical testers in an ordinary laboratory, and it is fortunate that a close relationship exists between the viscosity of an oil and its characters as a lubricant. In other words, if a given oil is satisfactory under known conditions of fit, pressure, speed, and temperature, it may be predicted with tolerable certainty that another oil of the same nature, having a similar viscosity, will yield equally good results.

The one serious drawback in this deduction is that it only holds true with oils from the same, or similar, crudes. The tests of an oil made from Texas crude may be exactly the same as those made from a Franklin (Pa.) crude, but will not do the same work. The nature of the hydrocarbons plays a most important part in the matter. For the foregoing reason it is impossible for a chemist to certainly predict the action of an oil from his tests unless he knows the stock from which it was made.

The characters which should be taken into consideration in forming an opinion on the suitability of a lubricating oil for a particular class of work are:

1. The viscosity or "body" of the oil at the temperature at which it is to be used.

2. The temperature at which the oil thickens or actually solidifies.

3. The flashing-point, or temperature at which the oil gives off inflammable vapour in notable quantity.

4. The volatility or loss in weight which the oil suffers on exposure in a thin film to an elevated temperature.

5. The "gumming" character, or tendency of the oil to become oxidised.

6. The proportion in which the fatty and hydrocarbon oils of a mixture are present.

7. The proportion and nature of the free acid, if any, in the oil.

8. The tendency of the oil to act on metals.

9. The presence of mineral matters, such as the bases of soaps.

10. The presence of graphite.

11. The presence of tarry matter.

12. The presence of metal particles in a recovered (filtered) oil. C. F. Mabery and J. H. Williams (*J. Amer. Chem. Soc.*, **30**, 992–1000 (1908)) have determined the relative lubricating values of corresponding members of the different series of hydrocarbons found

in petroleum. The following tables show some of the results obtained by Mabery and Williams. The hydrocarbon series having the least hydrogen were found to have the greatest viscosity and lubricating value. This had been known in a general way from practical experience. For instance, it has been known for some time that the viscosity of melted paraffin was much less than hydrocarbons of the same b. p. of series lower in hydrogen. This work of the above-mentioned authors is quite detailed in its proof and is of great commercial importance. Table A shows comparisons of sp. viscosity in two cases between higher and lower series, and table B similar results, with actual friction tests in addition.

TABLE A (60°).

Series	B. p.	Sp. gr.	Sp. vis.
C_nH_{2n+2}	294–296° (50 mm.)	0.781	10.88
C_nH_{2n-2}	294–296° (50 mm.)	0.841	21.23
C_nH_{2n+2}	274–276° (50 mm.)	0.775	8.51
C_nH_{2n}	274–276° (50 mm.)	0.835	15.63

Viscosimetry.—As already stated, the viscosity or "body" of an oil is the most important criterion of its suitability as a lubricant under certain conditions, and hence great interest attaches to its satisfactory determination. It has acquired greater importance of late years, owing to the rapidly increasing employment of mineral lubricating oils as substitutes for the fatty oils formerly used. Thus, different specimens of any given fixed oil, such as sperm oil or rape oil, vary in viscosity only within comparatively narrow limits at a given temperature, and hence an engineer accustomed to use a given fixed oil would, in purchasing such oil, derive little advantage from a knowledge of the viscosity of a particular sample of such oil. On the other hand, mineral lubricating oils may be manufactured of any required viscosity within comparatively wide limits, and hence it is very important that an engineer should be able to ascertain whether further supplies of this class of lubricant are of a viscosity similar to that of the oil previously employed.

It was formerly assumed that the viscosity of an oil bears a tolerably

TABLE B.—COMPARATIVE LUBRICATING VALUES OF HYDROCARBON SERIES.

Oil treated	B. p.	Sp. gr.	Sp. vis. 20°	Test of durability mins.	Temp.			Coef. of friction		
					Start	2 hrs.	Break	Start	2 hrs.	Break
Hydrocarbon C_nH_{2n} ...	274–276° (50 mm.)	0.861	37.57	120	76°	107°	124°	0.02	0.01	0.015
Hydrocarbon $C_nH_{2n} - 2$	312–314° (50 mm.)	0.868	88.16	150	80°	130°	185°	0.01	0.02	0.02
Hydrocarbon $C_nH_{2n} - x$	228–230° (30 mm.)	0.923	94.3	210	75°	113°	164°	0.03	0.01	0.01
			Viscosity.							
Castor	....	0.97	104 (210°)	150	70°	165°	225°	0.04	0.025	0.03
Sperm	....	0.94	192 (90°)	140	70°	120°	160°	0.02	0.01	0.01
Rape	....	0.91	108 (150°)	120	80°	160°	230°	0.03	0.02	0.05
Cylinder oil (comp.)	....	0.92	123 (212°)	75	80°	180°	210°	0.05	0.03	0.06
Cylinder oil (comp.)	....	0.89	135 (210°)	200	80°	185°	225°	0.07	0.03	0.06

definite relation to its sp. gr., but the fact that this is an error is now generally recognised.

Sherman, Gray and Hammerschlag show a comparison of the Calculated and Determined Viscosity Numbers (Engler) and Flashing and Burning Points in Oil Mixtures (*Jour. Ind. and Eng. Chem.*, **1,** 13 (1909)). In mixtures of 2 petroleum lubricating oils, or of a petroleum oil with a fatty or sperm oil, the Engler viscosity numbers and the flashing- and burning-points were invariably found lower than would be calculated from the percentages and properties of the constituents, if it were assumed that their properties were practically additive, like the sp. gr. In general, the difference between the calculated and observed values increases with the difference in properties in the 2 oils constituting the mixture. In some cases the differences were greatest in mixtures containing equal weights of the constituents, but more generally the difference was greatest in cases where a smaller proportion of the low-test or lighter oil was mixed with a larger proportion of the high-test or heavier oil.

Krause observed the following rates of flow at 15° for 4 varieties of mineral oil of identical sp. gr. (0.883):

Saxony oil (paraffin)......170 seconds	American...............550 seconds.
Oelheim................355 seconds.	Scotch..................585 seconds.

Temperature has much influence on the viscosity of oils, and is greatest in those which are solid or partly so at ordinary temperatures. The thicker animal oils containing much stearin are most sensitive to an increase of temperature. Many mineral oils, however, though fluid at ordinary temperatures, decrease in viscosity so rapidly when heated as to have quite different characters at high temperatures. This fact must be kept in mind when an oil is to be used in an engine cylinder or under similar conditions. As the temperature of a given friction surface is liable to vary considerably, preference should be given to an oil which shows the least variation in viscosity with the limits of temperature to which it is likely to be subjected.

The following figures by J. Veitch-Wilson show the decrease in viscosity by rise of temperature of certain typical fatty lubricating oils:

Oil	Number of seconds required		
	At 15.5°	At 49°	At 82°
Sperm.............................	47	30.5	25.75
Olive..............................	92	37.75	28.25
Lard...............................	96	38	28.5
Rape..............................	108	41.25	30
Neatsfoot.........................	112	40.25	29.25
Tallow (oil).......................	143	37	25
Engine tallow.....................	Solid	41	26.5

The following are figures obtained in Allen's laboratory:

Oil	Sp. gr. at 15.5°	Number of seconds required		
		At 15.5°	At 50°	At 100°
Sperm.........................	881	80	47	38
Seal (pale).....................	924	131	56	43
Northern whale.................	931	186	65	46
Menhaden.....................	932	172	40	....
Sesame........................	921	168	64	50
Arachis........................	922	180	64	....
Cottonseed (refined)............	925	180	62	40
Nigerseed.....................	927	176	59	43
Olive..........................	916	187	62	43
Rape..........................	915	261	80	45
Castor.........................	965	2420	330	60

Boverton Redwood (*J. Soc. Chem. Ind.*, 1886, 128) has determined by his standard viscosimeter (page 151) the comparative rates of flow of a number of oils for every rise of 10° F. The following figures are the number of seconds required for 50 c.c. of each oil to flow through an orifice out of which an equal measure of water at 60° F. ran in 25.5 seconds:

Temperature; °F.	Refined rape oil	Beef tallow	Sperm oil	Neatsfoot oil	American mineral oil, sp. gr. = 0.885	American mineral oil, sp. gr. = 0.913	American mineral oil, sp. gr. = 0.923	Russian mineral oil, sp. gr. = 0.909	Russian mineral oil, sp. gr. = 0.915	Russian mineral oil, semi-solid
50	712.5	......	......	620	145	425	1030	2040	2520	......
60	540	......	177	470	105	295.5	680	1235	1980	......
70	405	......	137	366	90	225	485	820	1320	......
80	326	......	113	280	73	171	375	580	900	......
90	260	......	96	219	63.5	136	262	426	640	......
100	213.5	......	80.5	175	54	111	200	315	440	1015
110	169	......	70.5	147.5	50	89.5	153	226	335	739.5
120	147	......	60.5	126	47	78	126	174	245	531
130	123.5	......	57	112	44.75	63.5	101	135.5	185	398.5
140	105.5	......	51	88.5	41	58	82	116	145	317.5
150	95.5	......	49	75.5	37.5	52	70.5	95	115	250
160	85	......	47.5	70	......	46	63.5	83.5	93.5	200
170	76	......	46	62	......	......	58	70.5	77.5	161
180	69	......	44.5	56.5	......	......	52.5	61.5	67.5	134.5
190	64.5	......	43	53	......	......	47	56.5	61	115.5
200	58.5	54.5	42	50.5	......	......	42	48	54	99
210	54	......	41	48.5	......	......	40	......	......	85
220	54	......	39	.47	......	......	38	......	......	77
230	47.5	......	37	46	......	......	......	......	......	70.5
240	45.5	......	36	44.5	......	......	......	......	......	64.5
250	43.5	40	35	44	......	......	......	......	......	59
260	Viscosity slightly above the average.	......	34	43.5						54
270		......	33	43						48.5
280		......	32	41.5						46.5
290		......	31	41						46
300		......	30	38						42.5

On examining the results recorded in the foregoing table, it will be observed that sperm oil is remarkable for the comparatively slight reduction in its viscosity caused by increase of temperature, a property to which the value of this oil as a lubricant for use under very varied conditions is probably due. The Russian mineral oils lose their viscosity with an increase of temperature more rapidly than American oils of the same sp. gr., but in both classes the reduction is most rapid in the case of the most viscous oils, and, as the Russian oils have a higher viscosity than the American, a more rapid reduction in the former case might be anticipated.

The elementary form of apparatus for determining viscosities consists of a pipette drawn out to a narrow orifice at the lower end. The tube is supported in a vertical position and filled with the oil to a certain

mark, the orifice being closed by the finger. The oil is then allowed to flow out till a lower mark is reached, or till a definite measure has been received in a graduated vessel, the number of seconds required being noted.

The viscosity of oils being affected to an important extent by very slight variations of temperature, it is very desirable to surround the viscosity tube with an outer tube or cylinder containing water at the desired temperature; for high temperatures a less volatile liquid than water might be substituted.

It is desirable in all cases to compare a sample of oil with others of known quality and origin, as the viscosity figures obtained by the use of one apparatus of the above kind are not directly comparable with, or even capable of strict conversion into, those yielded by others.

The viscosities are often stated as the number of seconds required to run through a certain orifice at a given temperature, and to render such figures comparative, they have usually been referred to rape oil as a standard. As, however, different samples of rape oil differ sensibly in viscosity, the results obtained by different observers have, for this and other reasons, not been capable of accurate comparison.

If, however, a defined and constant apparatus be employed, it becomes a simple matter to refer different samples to a standard. Water possesses too little viscosity to make it a desirable liquid with which to compare lubricating oils. Glycerol can be diluted with water to any required viscosity, and the sp. gr. of the standard liquid being once ascertained, a fresh standard can always be prepared at will. It is evident, however, that if the viscosity of rape oil be determined by the careful testing of a number of specimens, the average can be regarded as the viscosity of a standard rape oil, and if a constant apparatus be employed, the results can always be expressed in terms of such standard. Redwood has determined the viscosity of a considerable number of samples of genuine rape oil, and finds that the average time required for 50 c.c. of the oil at 15.5° to flow out of a Redwood's viscosimeter is 535 seconds, water under similar circumstances running out in 25.5 seconds. Taking, therefore, the viscosity of standard rape oil at 100, the viscosity of any other oil of the same density will be found by multiplying by 100 the time in seconds required for 50 c.c. to flow through the orifice, and dividing the product by 535. If the density of the sample be different from that of rape oil, the figure thus obtained should be multiplied by the sp. gr. of the sample at the temperature

of the experiment, and divided by 915 (the sp. gr. of refined rape oil at 15.5°). The rule is expressed by the following equation:

$$\frac{\text{Seconds of flow} \times 100 \times \text{sp. gr. of sample}}{489525} = \text{Viscosity.}$$

Redwood's Viscosimeter.—Boverton Redwood devised an instrument (Fig. 6) which is capable of being standardised, and has been much
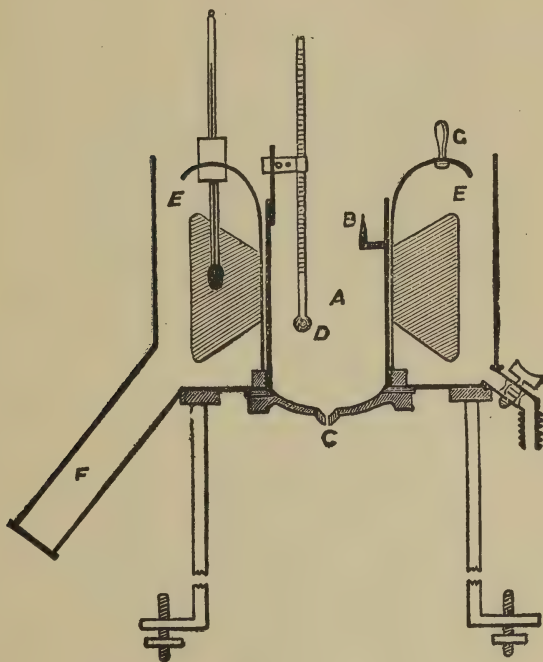
Fig. 6.

used. The viscosity tube (A) is made of copper thickly electroplated, and is 3 1/2 in. high by 1 7/8 in. internal diameter. In practice it is filled until the surface of the liquid just touches the point of a bent wire soldered to the side of the tube. The orifice is a hole of a definite size drilled in agate (c), but glass might doubtless be substituted without affecting the accuracy of the indications. The friction of the flowing oil against the sides of a long tubular orifice notably affects the

indications of the instrument, and hence the tubular portion of the orifice is made as short as practicable. The upper surface of the agate is cup-shaped, so as to fit the bulb of the thermometer (D), which may be used as a plug, but the instrument is also supplied with a spherical plug of electroplated copper attached to a wire. The viscosity tube is surrounded by a cylindrical reservoir of copper (E), which can be filled with water or other fluid and readily brought to and maintained at any desired temperature. For temperatures below 100°, water is most convenient; above that temperature, paraffin or mineral lubricating oil of high b. p. may be used. The fluid in the reservoir may be heated by a gas-flame placed under the projecting portion (F), and can be agitated by gently moving the inclined paddles by means of the handle (H). When the temperature employed is considerably above that of the laboratory, the agitator should be kept in gentle motion throughout the experiment. Care must also be taken that the temperature of the oil in the inner cylinder is maintained constant, as a difference of 1° or less will make an appreciable difference in the rate of flow of some oils.

In using Redwood's viscosimeter, the liquid in the reservoir should first be brought to the required temperature, and the oil to be tested, previously brought to the same temperature, should then be poured into the inner cylinder until the level of the liquid just reaches the point of the gauge (B). A narrow-necked flask, holding 50 c.c. to a point marked on the neck, is placed beneath the jet in a vessel containing a liquid of the same temperature as the oil. The ball-valve is raised, and the number of seconds required for 50 c.c. of the oil to flow out is noted in the usual way. At least two experiments should be made, and the results should agree closely.

Samples should be filtered if not quite clear, as suspended matter or globules of water may obstruct the orifice. Soft paper should be used for wiping out the oil-cylinder. In employing this or similar forms of viscosimeters, it is essential that the oil should be at the same height in each experiment, and that the same measure should flow out, otherwise discordant results will be obtained. Allen made an addition to the Redwood's viscosimeter by which a constant head of oil is maintained. The oil-cylinder is provided with an air-tight cover. The cover is perforated by 2 holes fitted with short tubes, one of which is furnished with a tap, while the other has another tube screwing air-tight into it. This tube (C) is prolonged on 2 sides in contact

with the agate orifice, while the angles of the inverted V-shaped slits cut on each side terminate exactly 1 1/2 in. higher. The cylinder is filled with oil before commencing an experiment, the tap closed, and the orifice opened till the oil sinks to a certain level in the inner tube. Air then bubbles in regularly, and when this is noted, the oil is collected in a graduated cylinder. Any volume from 10 to 50 c.c. may be
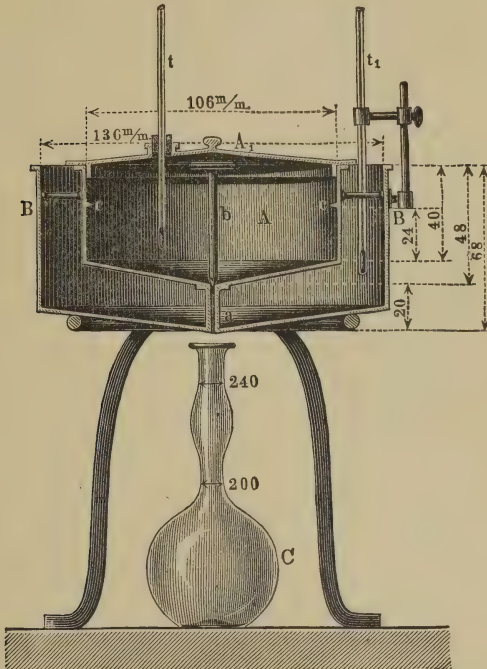
FIG. 7.

allowed to run out, as the oil gradually falls in the upper part of the cylinder, but is maintained constantly at the level D. Experiments made in Allen's laboratory prove the flow to be extremely regular; and the modification has the additional advantage of allowing the viscosity to be determined from the flow of a very moderate measure of oil, whereas if 50 c.c. be the volume collected, the observation sometimes becomes tedious. The results obtained by comparative testing by the closed and open apparatus agree.

Engler's viscosimeter consists of an accurately made brass oil-vessel 106 mm. internal diameter, 40 mm. deep at the side, and 48 mm. at the centre, the bottom being a flat cone. A slightly conical lid, fitting snugly like a saucepan-lid, closes the vessel. The inner surface of the oil-vessel is gilded. In the centre of the bottom is a platinum outflow tube 20 mm. long, with a slightly conical caliber 2.9 mm. at the top, 2.8 mm. at the lower end. This tube can be closed by a pointed rod of hard wood. The level to which to fill the oil (240 c.c. are used) is indicated by three small pointed projections on the side of the oil vessel. A thermometer passing through a hole in the lid dips into the oil. The oil vessel is surrounded by an oil-bath 130 mm. in diameter, 58 mm. high at the sides, and 68 mm. at the centre, at which latter point the lower end of the outflow pipe passes through by a tight joint. The top of this bath is on a level with the top of the oil-vessel. The bath is not covered; a thermometer dips into the oil. The whole apparatus is securely supported and heated by a ring burner. A flask marked at 200 c.c. and 240 c.c. is placed precisely below the outflow tube. To secure uniformity and obtain comparable data standardised instruments must be employed, for the construction of which Engler has arranged with Desaga, of Heidelberg. Full directions for use are furnished with each apparatus. This viscosimeter is much used in Germany, especially in the railway service.

Torsion Viscosimeter (*J. Amer. Chem. Soc.*, 1883, 173, 454).— This instrument depends on the principle of the torsion balance. It was devised by O. S. Doolittle for use in the laboratory of the Philadelphia and Reading Railroad Company. It has been found very satisfactory, and has been much used in American laboratories.

A steel wire is suspended from a firm support and fastened to a stem which passes through a graduated horizontal disc, thus allowing the torsion to be exactly measured. The disc is adjusted so that the index points to zero, showing that there is no torsion in the wire. A cylinder, 2 in. long by 1 1/2 in. in diameter, having a slender stem by which to suspend it, is then immersed in the oil and fastened by a thumb-screw. The oil is surrounded by a bath of water or paraffin, according to the temperature at which the observation is to be made. This temperature being observed while the disc is resting on its supports, the wire is twisted 360° by means of the knob at the top. The

disc being released, the cylinder rotates in the oil by reason of the torsion of the wire. The action is analogous to that of the pendulum. If there were no resistance to be overcome, the disc would revolve to zero, and the momentum thus acquired would carry it again to 360°. In reality, the resistance of the oil to rotation causes the revolution to fall short of 360° in proportion to the viscosity of the liquid. The retardation thus produced is a delicate measure of the viscosity.

There are a number of ways in which this retardation may be read, but the simplest is the number of degrees retardation between the first and second complete arcs covered by the rotating pendulum. For example, suppose the wire be twisted 360° and the disc released so that rotation begins. In order to obtain an absolute reading which shall be independent of any slight error in adjustment, the start from 360° is ignored, and the first reading taken at the end of the first swing. The next reading, which is on the other side of the O point, is also ignored, as it belongs in common to both arcs. The third reading is taken, which will be at the end of the second complete arc and on the same side of the O point as the first reading. The difference between these 2 readings will be the number of degrees retardation caused by the viscosity of the oil. Suppose the readings are as follows:

First reading.............right hand,	355.6°
Second reading...........left hand—ignore	
Third reading ....right hand,	338.2°
	17.4° retardation.

In order to secure freedom from error, two tests should be made—one by rotating the milled head to the right and the other to the left. If the instrument is in exact adjustment, these results will be the same; but if it is slightly out, the mean of the two readings will be the correct reading.

In order to overcome the variations in different instruments, each one is standardised against pure cane-sugar solutions, and the viscosity is expressed in the number of grm. of pure cane-sugar contained in 100 c.c. of the syrup at 15.5°, which will give the retardation designated at 26.6°. These readings are obtained by making a number of solutions containing known amounts of pure cane-sugar, and determining the retardation of each. A curve is then marked out on a piece of blotting-paper, the number of grm. of sugar in 100 c.c. of the

different syrups representing the abscissas, and the degrees of retarda-
tion the ordinates.   This curve enables us to interpolate the value of
each degree of retardation in terms of pure cane-sugar, and in this
way a table of viscosities is drawn up and furnished with each instru-
ment.   This table renders the results obtained by the different instru-
ments strictly comparable.

One advantage of the torsion viscosimeter is that the observations
are independent of the sp. gr. of the liquid, which is not the case with
instruments depending on flow.   Doolittle, in fact, found that liquids
of the same viscosity, but different gravities, gave markedly different

results with Saybolt's viscosimeter.
Tables showing comparisons between
viscosities determined by the Saybolt and
Doolittle apparatus are furnished by the
makers of the latter form.
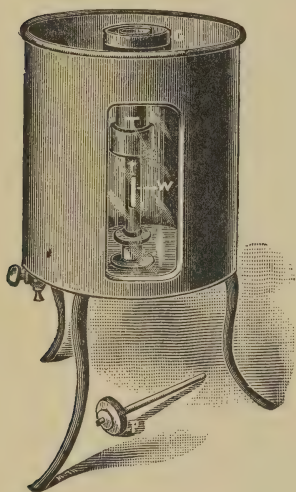
Among other advantages, the instru-
ment permits of the taking of viscosities
at high temperatures without the incon-
veniences of handling the hot liquid.
This is an important point, as the results
obtained below 100° are often so much
changed at higher temperatures that the
relative viscosities of two oils compared at
100° may be reversed when compared at
175°. (See page 148.) By means of a
paraffin bath these high temperatures can
be easily employed in this instrument.

FIG. 8.

When an oil has been tested, it is only
necessary to remove and wipe off the cylinder, when it is ready for
another test.   The data are also independent of any moderate amount
of dirt in the oil.

Saybolt's viscosimeter is much used in the United States.   It is
made in 3 forms, adapted for testing different grades of oils.   One
form consists of an outer vessel serving as a bath, and inner tube to
carry the oil.   In each of these there is a glass window, that the time
when the level of the oil reaches a certain point can be readily observed.

At the top of the oil tube there is a series of holes which open into
a trough, so that the tube cannot be filled above the line of these holes;
hence the same amount is used each time.   For higher temperatures

an apparatus is used without windows, the oil being allowed to flow into a flask marked at a definite volume.

Many other forms of viscosimeter have been devised or proposed. Most of them are based on the rate of flow under the influence of gravity, and hence are different only in details from the Redwood, Engler, and Saybolt instruments. Traube[1] has suggested a form in which the oil is forced by pressure through pipettes, the caliber of which differs according to the oil to be tested. Wright and Gill have expressed favourable opinions of this instrument, but it has not come into general use. Several forms have been constructed in which a vane is rotated in the oil, but with such apparatus it is very difficult to obtain uniform results. It is probable that the torsion instrument comes more nearly to the conditions of practice than any other form.

Cold Test.—Lubricating oils are subjected to this test with a view of deciding how well they can withstand low temperatures, without depositing paraffin or solidifying.

There are several forms of apparatus used for this test such as

    1. Chilling in a 1-in. test-tube.
    2. Chilling in a 4-oz. oil sample bottle.
    3. Refrigerator testing, such as in the Tagliabue apparatus.
    4. Testing in U-tubes with air pressure.

The first 2 simple forms of apparatus are much used. Probably the use of the oil sample bottle has preference, as it is available in all laboratories where oil is tested and is about of the right diameter and stronger than test-tubes. The refrigerator method is used in many of the best equipped laboratories, while the U-tube method is considerably used in Germany and elsewhere on the Continent.

    1. **Chilling in Test-tube.**—If tested singly or a few at a time, the oil is added until the tube contains about 1.5 in. in the bottom and placed in an ice and salt mixture for 1 hour and then warmed slowly at room temperature until the oil begins to flow on inclining the tube. This point is taken as the cold test. The oil is stirred with the thermometer to prevent taking low figures while the bulb is in a supercooled portion. With dark coloured oils, especially cylinder oils, the reading of the thermometer is liable to become obscured by the oil, which the operator must obviate by rubbing the thermometer against the side of the tube or else using a rod or something of the kind to rub the oil from the thermometer at the point of the mercury level. At

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[1] *J. Soc. Chem. Ind.*, 1887, 414.

least 2 tubes should be used for each test and the results averaged. In some cases frames are used to hold 8 or more tubes at once. In this case a liquid surrounds the tubes that freezes below the freezing-point of the oil, such as a brine solution and a freezing mixture surrounding this. The tubes after having cooled sufficiently, say for 1 hour, can be examined separately at room temperature as when 1 or 2 are done at a time.

2. **Chilling in Oil-sample Bottles.**—This procedure is exactly the same as is followed with test-tubes. About 1.25 to 1.5 in. of oil are used in the bottle.

3. **Refrigerator Testing.**—This method is prescribed by the New York Exchange and seems to be best carried out by the Tagliabue tester, which is a double-walled refrigerator. The oil is contained in a glass that is rocked, and the freezing of the oil can be noted through a window in the walls of the chamber.

4. An example of method 4 is the Schultze apparatus, which is described in Redwood as follows: The cold-test apparatus of Schultze, of Berlin, adopted by the Prussian State Railways, is fitted with a U-tube 6 mm. in diameter, and graduated in millimetres to contain the oil to be tested. The U-tube is immersed in a freezing mixture, and is connected with a manometer, by means of which, on opening a pinch-cock, a pressure equal to a height of 50 mm. of water may be applied to its contents. The temperature of the freezing mixture is indicated by a thermometer, and may be adjusted as required by varying the constituents of the mixture. In applying the test, the U-tube, charged with the oil to a height of 30 mm. in each limb, is immersed in the freezing mixture for an hour, after which it is raised so that the oil surface is above the refrigerant. The pressure from the manometer is then allowed to act, and the rate at which the oil is depressed in the limb connected with the manometer, during 1 minute, is noted. Several U-tubes containing samples of oil may be cooled simultaneously, and tested one after the other.

The flashing-point, or temperature at which an oil gives off a notable quantity of *inflammable vapour*, may be determined by the methods given on pages 120 *et seq.* The flashing and b. p. of the fatty oils are so high as to be beyond the temperature to which they are subjected in use; but with hydrocarbons the point becomes important. In the case of oils employed for engine cylinders, the flashing-point should certainly not be lower than 200°, nor the burning-point below

260°. The importance of a high flashing-point is twofold in such cases. There is less chance of inflammation, and the india-rubber packing of the cylinders is less liable to be injured. Undoubtedly the greatest value of the flash and fire tests lies in their indication of the relative density or body that two oils, under comparison, may have.

The loss by heating the oil is also an indication of the presence of volatile constituents, which may cause a serious increase in the amount of oil consumed in practice. To observe the behaviour of the oil, a known weight should be placed in a watch-glass, wide beaker, or flat porcelain dish, and kept for 24 or 48 hours in an air-bath at a temperature similar to that to which it will be exposed in practice, and the residual oil weighed. Gill heats the oil for 8 hours, and regards a loss of over 4% as sufficient to condemn the oil.

The drying character of an oil may be indicated by the test last described, the increase in the weight of different samples when exposed under the same conditions being a measure of their tendency to oxi-dise, providing they do not lose volatile constituents. As they prob-ably will lose such constituents this test is of little value, and the oxygen-absorption test, described below, must be used. The method of making the test may be varied. "Gumming," or tendency to dry, if existing to any notable extent, renders an oil unfit for use as a lubricator. The hydrocarbon and terrestrial animal oils are prac-tically free from drying tendencies; but "fish" oils are less perfect in this respect, with the exception of sperm and bottlenose oils, which have peculiarities which distinguish them from all others (see Vol. 2, page 240). The vegetable oils differ greatly in their drying prop-erties, but even the so-called non-drying oils, like rape and olive (see Vol. 2), are not wholly free from a tendency to thicken. An admixture of hydrocarbon oil notably reduces the tendency of a vegetable oil to thicken, and correspondingly diminishes its liability to generate sufficient heat to cause spontaneous combustion. On the other hand, the presence of resin causes a notable increase in the gumming tendency of an oil.

For determining the gumming quality of lubricating oils, A. Bach (*Chem. Zeit.*, 1889, **13**, 905) uses the following method, slightly modified from that of Fresenius:

The oil is heated for 10 hours with oxygen in a sealed tube (about 100 to 125 c.c. capacity) in an air-bath; the point of the tube is then broken under a measured volume of water, and from the difference in

volume the absorption is calculated. The presence of excess of oxygen after the completion of the experiment should be proved with a glowing splinter of wood. The following absorptions were obtained, 1 grm. of oil being taken in each case:

	Oxygen absorbed
Mineral oils..	0.1 to 0.7
Mineral oils (0.865)..	4.8
Lubricating grease...	21.8
Cod oil (0.963)..	76.3
Rosin oil..	181.0
Olive oil..	144.0
Rape oil..	166.0
Cottonseed oil	111.0
Mineral oil (0.865) with 10% cod oil.......................	9.4
Oleo-naphtha with cod oil..................................	8.6

Rosin oil or vegetable oils in admixture with mineral oils can thus be detected on account of the low oxygen absorption of the latter. Further, the oil has only a slight or no acid reaction in the case of mineral oil, and a strongly acid reaction in that of rosin oil.

The free acid of an oil and its tendency to *act on metals* are characters which are closely related. A perfectly neutral oil has no action on metals at ordinary temperatures, and experiment shows that the corrosive action increases in direct proportion with the quantity of free acid present (Vol. 2, page 9).

Many cases of so-called "clogging" or "gumming" of oils, commonly attributed to oxidation, are really due to the action of the free acids on the metal bearings of the machinery, with consequent production of soaps. The corrosion of bearings by oils has not received the attention it deserves, as the wear and tear of the metal and the thickening of the oil have been attributed to other causes. Liquid oils appear to corrode metals very evenly, so that the effect is not readily observed, but with solid fats it is very different.

Although *when freshly manufactured* an oil may be free from any trace of acid, it is not unlikely to acquire a very sensible acidity in time. This is true of many animal and vegetable oils, which have a tendency to become acid by keeping, through a partial splitting up of the fats into glycerol and free fatty acids. Hydrocarbons are free from this tendency, but it must be remembered that a hydrocarbon

which has been overrefined by means of sulphuric acid may develop serious acidity by keeping or by exposure to heat.

The presence or formation of free acid in an oil being the chief if not the only cause of its tendency to act on metals, the results published by various observers, showing the amounts of iron and copper dissolved in equal times by different oils, have no interest or meaning apart from the particular samples of oils examined, the action on the metals being simply a function of the free acid the oils happened to contain.

Although at the time of using, an oil may be wholly free from acid reaction, it may, if of animal or vegetable origin, readily become acid, and hence corrode the metallic surfaces it is employed to lubricate. This is notably the case when the oil is exposed to the action of high-pressure steam, as under such conditions all the fatty oils suffer decomposition more or less readily, with formation of free fatty acids and glycerol.

The free fatty acids formed by the hydrolysis of the oil readily act on the metal of the cylinder and produce an iron soap which clogs up the machinery in a very troublesome manner. It is a curious fact that the soaps of iron and other of the heavy metals (especially the oleates) are soluble in hydrocarbons, though insoluble in water, the reverse being the case with the soaps of the alkali metals. As a consequence of this the iron soap produced in engine cylinders lubricated with tallow, castor oil, or other fatty oils, becomes dissolved out whenever a change is made to a mineral lubricating oil. This fact is well known to engineers, but it has often been wrongly attributed to an abundant production of "gummy matter" by the mineral oil itself.

In some cases it is found difficult to obtain mineral oil having a sufficiently high viscosity at the temperature at which it is intended to be employed, and an addition of castor oil is consequently made. There then arises the practical inconvenience that mineral and castor oil are mutually soluble only to a very limited extent, but by addition of some other oil, such as tallow oil, perfect union can be effected. The "blown oils" now extensively manufactured as substitutes for castor oil are readily miscible with mineral oil.

A mixture of mineral oil with fatty oil, when used in an engine cylinder, appears to exert a less corrosive action on metals than might be anticipated from the proportion of fatty oil in the mixture, the mineral oil appearing to prevent the decomposing action of the steam on the fatty oil.

It is evident from the foregoing considerations that, in making an examination of a lubricating oil, its tendency to act on metals should be tested as far as possible under the circumstances and at the temperature of its use in practice. Thus, not only should the nature and proportion of free acid present in the original oil be ascertained, as described in Vol. 2, page 9, but in some cases this determination should be supplemented by a titration of the oil after it has been exposed to a high temperature in contact with water. 50 grm. of the oil and an equal measure of water should be heated in a closed bottle immersed in boiling water. The contents are frequently agitated, and after 6 or 8 hours the bottle is opened and the oil and water are separated. They are then titrated separately with decinormal alkali, first using methyl-orange as indicator to show the presence of mineral acid (sulphuric) and then phenolphthalein to show the presence of other acids. The acidity of the aqueous liquid will generally be due to *free sulphuric acid*, produced by the decomposition of sulphonates in the original oil, and if found in notable quantity, proves the oil to be of an objectionable character. The acidity of the oily stratum and that indicated with phenolphthalein in the aqueous layer will represent the fatty acids formed by the action of the water, *plus* the fatty acids previously present, which latter can be ascertained by titrating the original oil. In the case of cylinder oils, it may sometimes be desirable to heat the oil and water in a sealed tube contained in a bath of boiling saturated solution of calcium chloride, which will give a temperature corresponding to an internal pressure of 10 atmospheres, or about 150 pounds per square in., but in most cases a temperature of 100° will suffice.

Useful results can be obtained by exposing to the air samples of lubricating oil in flat porcelain dishes. Bronze coins or coils of copper or iron wire are partially immersed in the oils. When copper is employed, in the course of a day or 2 many samples of oil acquire a bright green colour from dissolved copper oleate, but in other cases the extent of the action is much disguised by the brown colour of the oil. If the oil be transferred to a separator and shaken with ether and dilute sulphuric acid, the dissolved metals pass into the acid liquid. On separating this from the ethereal layer and adding excess of ammonium hydroxide, the depth of the blue colouration produced is a fairly accurate measure of the action of the oil on the copper. If iron wire has been employed, the depth of the red colouration pro-

duced by adding a thiocyanate instead of ammonium hydroxide, will serve to indicate the extent of the action. The method, which is due to Archbutt, is capable of being applied quantitatively, and gives useful comparative results when employed under constant conditions.

In some cases useful results are obtainable by exposing oils in contact with metals at an elevated temperature, and then ascertaining the extent of the action as just described.

W. Fox (*Analyst*, 1883, **8**, 116) considers that the value of a non-mineral lubricating oil is inversely as its tendency to absorb oxygen when heated to 100° in contact with a metal, such as finely divided lead. His figures show, however, that the drying tendency of the oil employed is the chief factor concerned, though the amount of oxygen absorbed is not an accurate criterion of this property.

Mineral matters can be detected in the residue left on igniting the oil. *Free alkali* can be estimated by titrating the oil in presence of alcohol with standard acid and phenolphthalein, and that existing as *soap* by using methyl-orange as an indicator. *Aluminum palmitate* and *oleate* are now added to mineral oils to increase viscosity. Various soaps, especially those of aluminum, are added to lubricants to increase the viscosity. A mixture of mineral oil with about 10% of aluminum soap is sold largely under the misleading name "gelatin."

For the detection of these Schweitzer and Lungwitz (*J. Soc. Chem. Ind.*, 1894, **13**, 1178) have devised the following test: About 0.5 c.c. of the sample are dissolved in 5 c.c. of petroleum spirit (boiling below 75°), anhydrous ether or absolute alcohol, and mixed with 1 c.c. of a saturated solution of metaphosphoric acid in absolute alcohol or anhydrous ether. In the presence of potassium, sodium magnesium, or aluminum a precipitate is formed. The reaction depends on the fact that, while metaphosphoric acid is soluble in absolute alcohol or ether, most of its salts are insoluble. The reagent may be prepared by shaking the powdered metaphosphoric acid with absolute alcohol, allowing the mixture to stand until clear, and pouring off the solution. It must be kept tightly stoppered.

Calcium oleate is not infrequently added to, or formed in, mineral lubricating oils. (See Lubricating Greases.)

MINERAL LUBRICATING OIL.

The products classed under this title are obtained chiefly from two sources, namely, the less volatile fluid portions of petroleum and the

less volatile fluid portions of the oil produced by the distillation of bituminous shale. In the case of petroleum the lubricating oil has not always undergone distillation, but is obtained from the residues by treatment with charcoal and other purifying agents. Such oils, often called "natural oils," or "reduced oils," are preferable as lubricants to those which have undergone distillation.

The lubricating oil obtained from either American petroleum or shale has essentially the same chemical composition. It consists largely of the higher olefines, with, in the case of the shale product, small amounts of polymerised acetylenes, and possibly also terpenes. Small proportions of solid paraffines are often present in solution, but higher members of the series peculiar to Caucasian petroleum (p. 42) are probably present in large amount.

Mineral lubricating oils range in colour from pale yellow through all shades of red, brown, green, and blue, to black. The better qualities have very little taste and no marked odour, either at the ordinary temperature or when heated and are more or less bright in colour.

Mineral lubricating oils have sp. gr. ranging from 0.850 to 0.925, the most usual figures being between 0.880 and 0.910. An oil of sp. gr. 0.940 has been prepared from Brazilian petroleum. They are not optically active, but usually exhibit a strongly marked blue or green fluorescence, a characteristic in their detection.

The fluorescence or "bloom" of mineral lubricating oil may sometimes be destroyed by exposure to light, but more rapidly and certainly by subjecting it to a process of limited oxidation by treatment with nitric acid. Turmeric, α-nitronaphthalene, and picric acid also obscure the fluorescence. Dinitrotoluene is much used in the proportion of 4 pounds to the ton of oil. There are, however, varieties of mineral lubricating oil wholly non-fluorescent, and in which the property cannot be developed by any known treatment.

Mineral lubricating oil is not acted on by alkali, a fact on which is founded the process of detecting and estimating it when mixed with fat oils. (See page 10.)

When treated with bromine, mineral lubricating oils absorb a proportion of bromine which is of some value in forming an opinion as to the origin and constitution of the oil. (See page 93.)

An English patent has been granted for a mixture of soap, turpentine, and mineral oil of high b. p. It is claimed that by this means a

much larger proportion of paraffin oil can be added to soap than when turpentine is not used.

EXAMINATION OF MINERAL LUBRICATING OILS.

In determining the general character of hydrocarbon lubricating oils, as also their suitability for special purposes, the properties to be taken into account are the same as those which are important in the case of lubricating oils of animal or vegetable origin, but the following additional characters may be noted:

Colour is of little importance except for the fine kinds of oil. For choosing the best engine and cylinder oils it plays a very important part as it aids one in determining the nature of the stock from which they are made. It is well nigh impossible to bring Russian or Texas "reduced" oils by any process of filtering or acid treatment to the clear bright reddish colour, easily obtained in oils made from certain varieties of Pennsylvania crude, such as Franklin or Tiona. A well-marked fluorescence is an ordinary characteristic of mineral oils, but is in no respect a test of quality. Turbidity may be due to water in suspension, in which case the oil usually froths on heating, or it may be caused by the presence of solid hydrocarbons which dissolve on warming the oil. Other *solid matters* may be separated by diluting the oil with ether or petroleum spirit, filtering, washing the residue with ether, drying it gently, and weighing.

The odour should be very slight, even on warming. A marked odour indicates an imperfectly refined oil, or the presence of objectionable volatile compounds which will lower the flash-point of the oil and increase its waste in use.

The sp. gr. may vary within wide limits. As a rule, the greater the sp. gr. of an oil, the higher will be its flash-point and viscosity; but there are many exceptions. Lubricating oils from Russian petroleum have a higher viscosity than the products of similar density from American petroleum and shale oil. In the case of oils completely fluid at the ordinary temperature, the sp. gr. may be determined by any of the usual methods. The density of the thicker and semi-solid oils is best ascertained by filling a sp. gr. bottle to the brim with the warm oil. When it has cooled to a temperature of 15.5°, the stopper is inserted, and worked to and fro until it is forced home, the excess of oil gradually escaping through the perforation in the stopper, when the bottle may be wiped and weighed.

The Westphal balance is also much used for lubricating oils; another method is that of diluting alcohol until the oil neither sinks nor swims, and then determining the sp. gr. of the alcohol. For technical or refinery use, as with naphthas and kerosene, the hydrometer is chiefly used.

Cold Test.—On exposure to cold the oil should assume the consistency of a jelly or ointment, and the temperature at which it undergoes this change should not be inconsistent with the conditions under which it is to be used. (See page 157 for methods of determining the cold test of lubricating oils.) The lubricating oil from Baku petroleum bears exposure to a very low temperature (—20° F. in some cases) without becoming solidified or even depositing any paraffin. This peculiarity may be employed to distinguish Russian from American products.

The flash-point of a lubricating oil should be fairly high. A low flash-point indicates the presence of volatile constituents which will produce an odour, cause waste, and may possibly be dangerous. A high flash-point is often rigidly insisted on in the case of oils to be used in cotton mills or engine cylinders. The flashing-points of the pale Scotch oils from shale range from 130° to 180°, and of the darker oils and greases from 180° to 230°. These oils usually become viscous about 0°. The pale oils from American petroleum manufactured by the Thompson & Bedford Company flash from 166° to 230°, the sp. gr. ranging from 0.885 to 0.920. The black oils flash at temperatures ranging from 180° to 204°, according as the m. p. varies from —10° to —1°.

The same procedure is carried out for lubricating oils as for kerosene, slight differences exist in the forms of apparatus used. They are made to withstand high temperatures.

In general of 2 oils of about the same sp. gr., the one with the highest fire test is the better as it indicates more homogeneous stock and with substantially the same fire test the lighter oil is the better for the same reason.

These tests are not only designed to indicate the relative losses sustained by different oils on being used at high temperatures, but taken with the sp. gr. they throw some light on the grade of crude from which the lubricating oils are made.

The flash-point of lubricating oils is best observed by the Abel apparatus, but the water-bath must be removed and the interme-

diate air-bath filled with olive oil or melted paraffin wax. The apparatus is then heated on a sand-bath, and the flash-point of the oil observed in the usual way. The New York State tester is also used. Some operators use the open test. In fact, a porcelain crucible fixed in a sand-bath frequently serves the purpose of a tester very well, especially for cylinder oils.

In Europe the Pensky and the Pensky-Martens instruments are most used for determining the flash test of lubricating oils. These are closed testers and modifications of the Abel apparatus.

In the United States the open tester is almost universally used. The glass cup in which the oil is held is heated by radiation from a metal vessel into which the cup rests.

The Pensky high temperature instrument consists of a metallic oil cup, fitted with a stirrer, with a flexible handle and 2 thermometers, one with the bulb in the oil and the other in the vapour. A small flame is passed over the opening in the top until a flash takes place. If the 2 thermometers do not indicate the same temperatures, the mean is taken.

The Pensky-Martens Tester.—Redwood describes this apparatus as follows: The cover of the oil cup consists of 2 parts, viz., the portion joined to the rim, and an upper portion which revolves through a small arc. In each portion there are 3 orifices, the central one being twice the area of the 2 lateral ones. These orifices may be made to coincide or the openings may be completely closed, according to the relative positions of the 2 portions of the cover. The lower part of the cover is fitted with a vertical rod serving as a support to a tube. This tube can be rotated upon the rod by turning the non-conducting milled head at the upper end, and the action compresses a spring. At the lower end the tube is provided with an arm, which, by the action of the spring, is held against a vertical stud. A pin projecting downward from the arm engages with a slot in the revolving portion of the cover, and on turning the milled head the openings in the upper portion of the cover are brought over those in the lower portion. At the same time, a flange projecting from the edge of the revolving portion of the cover comes into contact with the oscillating test-jet, and this is depressed, so that at the same moment when the central openings coincide, the test-flame is brought to the orifice. On releasing the pressure requisite to turn the milled head, the openings in the cover are again closed by the action of the spring, and the test-

jet is brought back to the horizontal position by the weight at the opposite end. This weight is attached to a stem forming a screw-valve, by means of which the size of the test flame can be adjusted. The gas is supplied through a lateral tube forming one of the supports on which the jet oscillates, the other support consists of a small stud. In the lower part of the cover of the cup there is a socket for a thermometer, and in the centre of the cover, there is a tube through which the stem of the stirrer passes. This stirrer is provided with a pair of arms working in the oil, and a smaller pair in the vapour-space about the oil. It is revolved by means of a flexible wire stem. The oil-cup is furnished with a pair of hooks for convenience in removing it from the bath, when hot, by means of the forked holder shown. The heating vessel consists of a cast-iron air-bath with an annular chamber exposed to the flame, and a brass jacket, which serves to check radiation. The jacket is separated from the iron casting by a considerable space at the sides and by a distance of a quarter of an inch at the top. The oil-cup rests upon the jacket, and therefore does not come into contact with the cast-iron. Beneath the bath there is a disc of wire gauze which is fitted to a swinging arm, so that it may be turned aside, and the flame of a Bunsen burner allowed to impinge upon the bath, when a high temperature is required.

The temperature of the oil should rise at the rate of about 10° F. per minute. In employing this, or any other form of close-test instrument in the testing of lubricating oils, it is important that the samples should be free from water, as the presence of aqueous vapour in the upper part of the cup prevents the occurrence of the flash.

If the cover of the oil cup be removed, the apparatus may be employed as an open cup for determining the flashing- or igniting-point, a gas flame not more than 1/4 in. in diameter being used to produce the ignition.

Residue on Ignition.—On ignition, a mineral lubricating oil should leave no inorganic residue, or merely an insignificant trace (less than 0.05%).

Miscellaneous Tests.—The oil should be agitated in a test-tube with an equal volume of boiling water, and the tube then kept in the water-oven until separation occurs. The formation of a granular white layer at the junction of the two liquids indicates the presence of *resin*. If the liquid assume a milky-white appearance, the oil has been insufficiently washed after the final treatment with soda. *Alkali* is

often purposely left in an oil with the view of increasing its "body" or viscosity. This is effected by blowing air through the imperfectly washed oil. As the moisture is got rid of, the oil takes up the soda, while remaining perfectly transparent. Such oil is very prone to oxidise, and becomes turbid on exposure to air from absorption of moisture. It is also liable to change in colour. If a mineral oil be boiled in a large excess of water for 3 or 4 hours, the oil will be practically unaltered in colour if of first-rate quality.

If the oil be agitated with an equal volume of sodium hydroxide solution of 1.36 sp. gr., and the tube kept at about 55° until the liquids have separated, a precipitation of *tarry matter* indicates that the oil has previously been insufficiently treated with soda, and hence is liable to deteriorate in colour. A first-rate oil gives no trace of tarry matter when submitted to this test. The formation of a white emulsion with the alkali is due to an admixture of some *fatty oil*, *fatty acid*, or *resin*. A diminution in the bulk of the oil indicates the presence of *phenoloid substances*, which may be estimated by a quantitative application of the test.

Fatty oils may be detected and estimated with considerable accuracy by saponifying the oil and removing the mineral oil from the aqueous solution of the soap with ether. In the ordinary course of procedure, however, in very many cases troublesome emulsions are met with. The "Reviser" of this section has recently published a method, however, which obviates the difficulty (*Jour. Ind. and Eng. Chem.*, 1909, **I**, 479).

Saponify in a flask in the usual way with alcoholic potassium or sodium hydroxide or sodium or potassium alcoholate, and when the saponification is complete evaporate about half the alcohol unless the soap formed separates on cooling, in which case more alcohol should be added until it dissolves. If a short glass tube is used as air condenser, by the time the contents of the flask have boiled sufficiently about half the alcohol will have gone off. Add rather more than an equal volume of ether, and transfer by washing the contents of the flask into a separatory funnel. Now add water while slowly rotating the flask until after a separation of the layers no further turbidity occurs in the lower layer on adding more water. About 5 to 6 volumes of water are added in this way. Draw off the lower layer to another funnel and add more water and shake out with ether and separate, when both layers are clear. This extract may contain a little non-saponifiable oil and is added to the main body of the ether solution of non-saponifiable oil after the first

ether layer containing the bulk of the non-saponifiable oil has been washed 2 or 3 times with water to remove alcohol that was dissolved in the ether.

After washing free of soap and alcohol, this ether extract with the second ether extract is evaporated in a tared flask and weighed. The reviser has carried out this procedure for several months on the classes of oils mentioned above and has never had one troublesome emulsion. In most all cases there was practically no waiting necessary, as the layers separated perfectly in a few minutes. It does not matter how much free alkali is present.

·**Acid Tests.**—When 10 c.c. mineral lubricating oil are shaken with 4 c.c. of sulphuric acid of 1.73 sp. gr. at 15.5° for 2 minutes, it will remain unchanged or acquire simply a yellow tint if of good quality, but if the sample be imperfectly refined, or if *coal-tar oil* be present, more or less browning will ensue. On treatment with concentrated sulphuric acid, in the manner described in Vol. 2, page 58, lubricating oils from shale and petroleum at first develop a trifling degree of heat (3° to 4°), though on continued stirring a very decided increase of temperature is sometimes observed. *Rosin oil* usually causes a rapid rise of 18° to 22°, and with *coal-tar oil* the action is still more marked. *Fatty oils* rarely give a less rise than 40°.

If 10 c.c. of the oil be mixed with an equal measure of fuming nitric acid of 1.45 sp. gr., but little rise of temperature will occur with good mineral oil or shale lubricating oil, but great heat is produced by coal-tar oil. Rosin oil mixes quietly with the acid, and then suddenly evolves much heat. Methods for detecting adulteration with rosin oil are described under that head.

Deblooming Agents.—As a general preliminary test, Holde (*J. Soc. Chem. Ind.*, 1894, **13**, 906) advises the following: The clear oil is boiled for from 1 to 2 minutes in a test-tube with about 3 c.c. of concentrated alcoholic solution of potassium hydroxide. Oils containing nitro-compounds become blood-red or violet-red, and on warming the upper part of the tube where there are adhering drops of the alkaline solution, just above the main bulk of the liquid, these drops become at once reddish-violet. Holde has never observed the latter reaction with any oils not containing nitro-derivatives, but some fatty oils will produce on long heating a yellowish-red or blood-red in the body of the liquid, although the usual colour is a merely brownish.

For the detection of α-nitronaphthalene used as a deblooming

agent, N. Leonard (*Chem. News*, 68 (1893), 297) has devised the following method, depending upon the production of α-amidonaphthalene, which has a characteristic disgusting odour, similar to that of a decayed tooth.

A small quantity of the oil is gently warmed with zinc dust and dilute hydrochloric acid, and the mixture shaken from time to time. If α-nitronaphthalene be present, the odour of the amido-derivative will be noted. When the reduction is complete, the acid water is withdrawn by a separatory funnel. A portion of this liquid, neutralised by ammonium hydroxide, will give, with ferric chloride, a blue precipitate, becoming purple. The remainder of the solution may be rendered alkaline with sodium hydroxide and extracted with ether, the ether evaporated, the residue dissolved in a little alcohol, and to this solution a drop of a solution of sodium nitrite, acidified with acetic acid, is added. A yellow is produced, which is changed to crimson by hydrochloric acid.

Mineral oils are sometimes compounded with caoutchouc. For the detection of this, Holde (*J. Soc. Chem. Ind.*, 1891, 10, 390) advises the following: Ascertain the solubility by shaking 1 volume of the oil with 2 volumes of alcohol, benzene, or ether; precipitate the caoutchouc by treating the oil with a mixture of 3 parts ether and 4 parts alcohol. The precipitate is filtered out, washed, dried, and weighed.

The best test of a lubricating oil is a practical test in a machine journal. A number of machines have been constructed for this purpose.

Thurston's Tester.—This machine, the invention of Professor R. H. Thurston, of Cornell University, is widely known. The lubricant is placed on a journal, carried on the extremity of a shaft, sustained by journals, on a rigid stand. The driving is effected by means of a pulley to which a belt is connected. The shaft is driven at a speed corresponding with the work which the lubricant is to do, and has a counter at the end to indicate the number of revolutions. The journal, is grasped by bronze bearings, pressed together by a spring adjusted by a screw, and having its pressure indicated on a scale by a pointer. A thermometer indicates the heat produced during the test. The brasses and springs are carried by a weighted pendulum, so that the maximum friction of the dry smooth bearing will swing it into a horizontal position. The pendulum carries a pointer tra-

versing an arc which is so graduated that by dividing the reading by
the pressure indicated by the pointer, the coefficient of friction, when
the lubricant is placed on the bearing, may be found.

The following methods for the examination of heavy mineral oil
have been formulated by the Scottish Mineral Oil Association (*J.
Soc. Chem. Ind.*, 1891, 346):

Flashing-point.—The oil cup and cover of the ordinary "Abel"
flash-point apparatus is to be employed. The cup is filled with oil
in the usual manner, and the rate of heating is to be such that at least
15 minutes are taken in raising the temperature of the oil to 148.8°.

In the event, however, of a dispute arising as to the correct flashing
point of a heavy mineral oil, the question is to be decided by means
of the "Pensky-Martens" apparatus.

Viscosity.—The "Redwood" viscometer is that which is to be
employed in the determination of the viscosity of mineral oils. Ordi-
nary results are to be expressed—as the time, in seconds, which 50 c.c.
of the oil take to flow through the orifice at a temperature of 21.1°.

Setting-point.—This is determined in the following manner:
Into a test-tube having a diameter of about 1 1/4 in. the oil to be
tested is added to the depth of about 2 in., the tube is then immersed
in a freezing mixture, the oil being slowly stirred with a thermometer
until it has cooled down considerably below the temperature at which
solid paraffin first appears; the tube is then removed from the freezing
mixture, the oil constantly stirred with the thermometer, and the point
carefully watched at which the last trace of solid paraffin disappears.
This operation is repeated with the same sample of oil, until 2 experi-
ments give concordant results, the temperature so found being the
setting-point.

Special Characteristics of Lubricating Oils.—Holde (Untersuch.
d. Mineralöle und Fette) divides lubricating oils into the following
classes:

1. Spindle oils for textile machinery, under very light pressure, so
mobile oils are required. Engler degree[1] at 20 = 5–12, flash, Pensky
160–200°.

2. Ice machine—compressor oil-mobile. Engler degree at 20 = 5–7.
Cold test under —20° flash, Pensky 140°–180°.

3. Light machine, motor and dynamo oil, moderately viscous.
Engler degree 13–25, flash, Pensky 170–220°.

[1] The Engler degree for water is about 6 times the viscosity of water in the Engler
apparatus at 20°.

4. Heavy machinery oils. Engler degree 25–45 (in special cases up to 60), flask, Pensky 190–220°.

The foregoing oils viewed in a test-tube are coloured brownish-yellow to brownish-red, a few of the most expensive ones of groups 1–3 are almost colourless. Compressor oils are often artificially coloured violet-red. The cheaper kind of machine oils are opaque.

5. Dark railroad oils (summer oils). Engler degree at 20° 45–60, (winter oils) 25–45, flash, Pensky over 140°. Cold test (summer oils) under —5, winter under —20°).

6. Cylinder oils—highest boiling distillation products of syrupy to salve-like consistency, which at room temperature or several degrees above zero become thick or solidify. Engler degree at 50°–23–45. Superheated steam cylinder oils often have Engler degrees of 50–60 at 50°.

If these oils are either distilled or filtered with fuller's earth they are brownish-red and translucent, but if not distilled or filtered are greenish-black and opaque. By reflected light the American oils are mostly grey-green, the Russian oils bluish. The flash-points are according to quality from 220 to 315°. The better ones are over 260°.

Inner Friction.—Viscosimeters do not give results that are anything more than comparative. The figures given are not in terms of any dynamic unit, such as those of cm., grm., second (c. g. s.) system. Ubbelohde and others have contributed toward this end, and the formula of Ubbelohde is given herewith. The absolute inner friction of the oil particles is measured by the force necessary to pass a layer of oil of 6 sq. cm. surface over a surface similar a distance of 1 cm. at a rate of 1 cm. per second. For water at 20° this value called fe is 0,010164.

Ordinarily the specific viscosity of water is taken as 1 and oils compared therewith.

The experimental determination of the exact specific viscosity is carried out with capillary tubes which give somewhat truer values than a viscosimeter, such as the Engler.

The formula of Ubbelohde is x = S. 7.317. fe.
Where x is the desired specific viscosity.

S is the sp. gr. of the oil at the temperature of the determination. fe is the figure of Engler degrees of the oil.

As this formula is based on Engler's degrees which are not much

used in the literature, reference usually being made to the viscosity of water at the same temperature and in the same instrument, the following is given:

The formula for the calculation of the inner friction of an oil is

$$\mu = \frac{\pi p r^4}{8 v l} t = \frac{v s}{2.3 \pi l} \times \frac{1}{t}$$

μ is the *absolute inner friction*, p the pressure in grm./sq. cm., r the radius of the outflow capillary, l its length in cm., v the volume flowing out in c.c., t the time of flowing in seconds.

Acidity in lubricating oils may be due to free acid from compounded animal oil, sulphonic acids, due to imperfect refining, and traces of sulphuric acid.

Free mineral acid may be distinguished by the use of methyl-orange as an indicator, but it is not likely to be found in a commercial lubricating oil as it sometimes is in kerosene as the unsaturated compounds found in large quantities in many lubricating oils would be changed into sulphonic acids. (See page 160 for free acid tests.)

Rosin oil is detected in mineral oils by a method of Allen, which consists in dissolving a few drops of the oil in question in 1 c.c. of carbon disulphide solution of stannic bromide containing an excess of bromine.

According to Redwood, Prof. Finkener recommends the use of a mixture of 1 volume of chloroform and 10 volumes of alcohol of 0.818 sp. gr. for separating rosin oil from mineral oils. 10 volumes of this mixture (at 23°) will dissolve 1 volume of rosin oil from admixture with mineral oils without taking up any appreciable quantity of mineral oil.

A method for the quantitative estimation of rosin oil in mineral oils is given by P. C. M. Ilhiney (*J. Amer. Chem. Soc.*, 1894, **16**, 385–8) and based on the principle that the action of nitric acid on rosin oil converts it into a brittle red resin and does not act on petroleum hydrocarbons. This resin is not dissolved by petroleum ether, which removes petroleum products. The details of the method are as follows:

50 c.c. of nitric acid (sp. gr. 1.2) is brought to boiling in a flask of 700 c.c. capacity. The flame is then removed and about 5 grm. of oil (noting exact weight) is then dropped in. The flask is then heated for 15 or 20 minutes on the water-bath and then 400 c.c. of water added. When cold the contents of the flask is treated with petroleum ether which dissolves all mineral oils and leaves the altered rosin oil. The difference in weight between the mineral oil recovered and the oil taken, gives the amount of rosin oil in the sample.

LUBRICATING GREASES.

The tests under this heading are according to Gillette (*J. Ind. and Eng. Chem.*, 1909, **1**, 351).

In the analysis of a grease, the following points may be covered:

Consistency.

M. p.

Flash-point.

Content of free acid.

Amount and nature of soap.

Ash, not alkali, from soap, nature and amount.

Mineral filler, as graphite, talc, etc., nature and amount.

Content of unsaponified, but saponifiable animal or vegetable fats or oils, nature and amount.

Content of unsaponifiable mineral or hydrocarbon oil, nature and amount.

Content of water.

The methods used in the analysis of the grease are as follows:

Note first the odour and colour. These may give clues of the probable composition, and will show if the grease is perfumed with nitrobenzol or any other similar substance. Note the behaviour on melting. The grease should melt to a clear homogeneous fluid. The oil should not melt away from the soap, since in such a case after being in the feed cup some time, the grease may change in composition the oil running off the bearing and the soap staying behind.

The m. p. is the most important single determination, as will be seen in the discussion of the friction tests.

Ubbelohde[1] gives a method for greases melting below 100°. Gillette found the most satisfactory method to be the use of an open tube of 0.4 cm. internal diameter, and about 8 cm. long. This is stuck into the grease so that a plug of grease 1 cm. long is left in the glass tube. The tube is then attached by a rubber band to a thermometer so that the plug is beside the bulb. The thermometer with the tube attached is then immersed into a beaker of water so that the bottom of the plug is 5 cm. below the surface. The water is then heated at the rate of 3 to 4° per minute. When the m. p. is reached, the plug, which is under a pressure of 5 cm. of water, slides upward in the tube. Checks can be obtained to 0.5°.

[1] Holde, "Untersuchung der Mineralöle und Fette," Berlin, 1905, p. 209.

The effects of varying the different conditions of this test have been investigated by Gillette.

The consistency at 20° was determined by a Legler consistometer which consists of a pointed glass rod, bearing a pan for weights, and supported by a spiral spring.[1]

The grease was maintained at 20° for about an hour, and the total weight determined which was required to sink the rod into the grease exactly 1 cm. The spring was of such strength that it took 20 grm. to depress the rod 1 cm. in air, and this 20 grm. was subtracted from the total weight required, to give the consistency number. This varied in different commercial greases from 200 grm. to 4 grm. Readings could be checked to within 5% of their value. The instrument gave a consistency number for the pasty mass consisting of 50% stearic and 50% oleic acids, of 75–80 grm. All the weights must be on the pan before it is released, as the penetration is less if the weights are added while the rod is falling. The measurement of the consistency is a well-recognised part of the examination of a lubricating grease,[2] yet it has no direct bearing on the lubricating power. Its value lies chiefly in showing what sort of grease cup should be used for that particular grease, whether gravity, compression, etc.

The flash-point is taken in a 50 c.c. porcelain crucible filled with the grease, into which is stuck a bulb of a thermometer. The crucible is heated at 5° per minute on a sand-bath, and the flash determined by noting the temperature at which 3 mm. gas flame passed over the crucible at 2° intervals causes a flash to pass over the surface. The chief value of this determination is to give some idea of the grade of mineral oil used in compounding the grease.

The content of free acid is obtained by dissolving or disintegrating, if not completely soluble, 2.82 grm. of the grease in a neutral mixture of alcohol and ether containing phenolphthalein. The grease is then titrated with N/10 KOH to pinkness, each c.c. of alkali used equalling 1% of free acid, calculated as oleic. Most commercial greases run almost neutral, 0.5% being high, though as high as 6% has been found. Greases that contain unsaponified palm oil are especially likely to show free acid. The importance of neutrality is very great, because of the corrosion of the bearings by free acid.

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[1] *Chem. Ztg.*, 1884, **8,** 1657; *Chem. Ctrbl.*, 1884, **15,** 734. Benedict and Lewkowitsch "Oils, Fats and Waxes," 1895, Ed., p. 74.
[2] Benedict and Lewkowitsch, *Loc. cit.* Archbutt and Deeley, "Lubrication and Lubricants," 2d Ed., p. 162.

The estimation of the soap content may be made in several ways. The bases may be thrown as oxalates from a turpentine-benzene-alcohol solution by oxalic acid, after the method of Conradson,[1] and the soap content figured from the amount of base found. The soaps may be determined by Holde's method of decomposing the soaps by mineral acid, washing out the mineral acid, and titrating the fatty acids thus freed, and from the titration figuring the amount of soap.

The simplest and shortest method, however, in practically every case, is to ash the grease, titrate the Na_2CO_3, K_2CO_3, or CaO in the ash with acid, and calculate the soap content from the titration, 1 c.c. of $N/2$ acid being equivalent to

> 0.1612 grm. potassium stearate.
> 0.1535 grm. sodium stearate.
> 0.1520 grm. calcium stearate.

If the Liebermann-Storch rosin test shows the soap to be partly rosin soap and rosin oil is absent, this will give low figures, owing to the higher combining weight of abietic than that of stearic or oleic acids. In such a case, if extreme accuracy is required, the fatty acids of the soaps may be freed, and rosin estimated by Twitchell's method. Ordinarily this would not be required.

In the case of greases made with sodium or potassium soaps, the soap may be directly determined after extraction in a Soxhlet of the unsaponified and unsaponifiable fats with ether, by extraction of the residue from the ether extraction, with alcohol. With lime soaps this fails, owing to the large solubility of calcium soap in all solvents for fats, as well as its insolubility in alcohol. It would greatly simplify the analysis of greases containing calcium soap if some solvent could be found that would extract fats and oils without extracting any of the lime soap, in the same way that ether may be used to separate the fats and oil from the soap in a soda soap grease. In attempting to make an ether extract of a lime soap grease, we have repeatedly found from $1/4$ to $1/3$ the total lime in the ether extract, owing to the solubility of calcium soap.

Gasolene extracts nearly as much. Numerous experiments have been made with other solvents and mixtures of solvents, but no satisfactory one has been found. Ethyl acetate at room temperature dis-

[1] *Jour. Amer. Chem. Soc.*, **26**, 6, 705.

solves but little of the calcium soap, and the extract will give a fair qualitative idea of the nature of the oil used in compounding the grease.

If the grease is made up with a lead soap, the lead may be determined by decomposing the grease by boiling with a mixture of sulphuric and nitric acids, after the Neumann acid ashing method, and weighing the lead sulphate.

The nature of the base used in the soap may be determined by the usual methods, or more quickly and delicately by microchemical methods. A small amount is ignited on a porcelain crucible cover, the ash dissolved in dilute HCl and 3 drops of the solution put on a microscope slide. To the first drop is added a small drop of dilute H_2SO_4, and to the second a small drop of H_2PtCl_6. The third is evaporated to dryness over a micro-burner, and a drop of concentrated solution of uranium acetate, slightly acidified with acetic acid, is added. The 3 drops are then examined under the microscope. The first will show the characteristic sheaf-like groups of gypsum crystals if lime is present, or the fine white granular plates and rhombs of $PbSO_4$ if lead is the base used. The second will show the yellow octahedra of K_2PtCl_6 if potassium is present, while the third drop will show the tetrahedra of the double acetate of uranium and sodium, if we are dealing with a soda soap.[1]

The amount of ash other than alkalies from the soap may be determined by the difference between the total ash and the alkali found by titration. Greases contain from zero to sometimes 1% of adventitious dirt, iron and aluminum oxides, silica, etc.

In the case of a grease containing graphite, talc, etc., the mineral filler may be estimated directly after extraction with ether and then with alcohol, if we are dealing with an alkali soap, or in any case, by weighing the ash insoluble in acid. In the case of graphite, care should be taken to ash to a low temperature to minimise the oxidation of the graphite.

The unsaponified saponifiable matter, in the case of a grease made with an alkali soap, is best determined by saponification of the ether extract with alcoholic potash. The nature of the saponifiable may be found by evaporating off the alcohol after saponification, extraction of the unsaponifiable with ether, freeing the fatty acids from the

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[1] For a full description of these extremely delicate and rapid microchemical methods which are so valuable but so little known, see Behrens, Microchemische Analyse, or a series of articles by Chamot in *Jour. App. Microscopy*, Vols. 3, 4.

soap left behind, and taking the m. p., iodine number, and refractive index of the fatty acids, and thus identifying the fat from which the acids come. This is simple if only a single fat was used, but less so in a mixture. In most cases where a grease contains unsaponified saponifiable matter, it has been made by a partial saponification of the fat in question, and so the original grease may be saponified directly and the total fatty acids examined.

In a calcium soap grease, the soap may be decomposed by heating with a little dilute HCl, washing, saponifying the freed fatty acids with alcoholic soda, evaporating the alcohol and extracting the mixture of soda soap and unsaponifiable, which is now in the condition of a grease originally made with soda soap, with ether. This gives us the unsaponifiable, and we may proceed with the examination of the fatty acids in the soap as above. The unsaponifiable ether extract will consist of mineral or hydrocarbon oil, and the sp. gr., flash-point, and refractive index will show us the nature of the mineral stock. In a rosin-oil grease we may treat the mixture of rosin oil and mineral oil by any of the usual methods for quantitative separation or estimation, none of which, however, are very satisfactory.

The estimation of water in lubricating greases is usually made either by the delightfully simple method of "determination by difference" or by drying down to constant weight. Archbutt and Deeley[1] advocate drying at 105° to 110° until frothing ceases. Wright[2] drys at 105° till the weight is approximately constant at half-hour intervals of weighing. Hurst[3] drys at 220° F. to constant weight. Conradson[4] takes moisture by difference, but recognised the fact that some oil is volatile at 100°. Holde[5] says: "The old method of mixing a weighed portion with alcohol, heating till no more bubbles appear, cooling and weighing, only gives useful results in the absence of light volatile oils. More general is the application of the Marcusson xylol method.[6] By this method 6 greases gave from 1 to 6.3% water, the difference between checks on the same grease being 0 to 0.2%. By other methods the water content came from 0.5 to 2.2% too high."

[1] "Lubrication and Lubricants," p. 306.
[2] "Analysis of Oils and Allied Substances," p. 104.
[3] "Lubricating Oils, Fats and Greases," p. 281.
[4] Jour. Amer. Chem. Soc., 26, 6, 705, June, 1904.
[5] "Untersuchung der Mineralöle und Fette," 2d Ed., p. 213.
[6] J. Marcusson, 1904. "Bestimmung des Wasser- und Säurengehaltes von Schmierfetten," Mitt. K. Materialsprüfungsamt, 24, 48; "Von die Bestimmung des Wassergehaltes von Oelen, Fetten, Seifen, Harzen, u.s.w.," Mitt. K. Mater., 23, 58. See also Hoffman, Z angew. Chem., 21, 2095; Chem. Abstr., 3, 2, 158 (Jan. 20, 1909). See page 141 for description of method of distillation with naphtha.

Attention was first drawn to this by a series of greases rather high in water and content which were dried in the water-oven to an apparent constancy of weight, but lacked several per cent. of adding up to 100. On investigation it was decided that the water estimation was the weak point, and determinations were made by the xylol method, when the analyses added up well. Further work showed that though in this case the moisture estimations by drying were too low, in general drying to constant weight gives high results, as claimed by Holde.

To estimate the moisture in a lubricating grease, then, we first test it with anhydrous $CuSO_4$ if the grease is sufficiently light in colour. If water is present, or in the case of a dark grease, 10 grm. are weighed out on a balanced filter-paper, put the grease and paper in a 300 c.c. Erlenmeyer flask and cover with xylol. The xylol should be distilled from water and separated out from the water after clearing in a separatory funnel. The flask, connected with a dry condenser, is heated in a bath of cylinder oil, and the xylol and water slowly distilled off till the xylol comes over clear. The bulk of the water comes over with the first 10 c.c. of distillate. The distillate may be caught in a burette filled with water up to the lowest graduation, best with a few drops of xylol added to give the same meniscus as we will read, or in a receiver made like a funnel, with a graduated stem closed at the bottom, according to the method of Dean,[1] and allowed to stand overnight, or until all milkiness had disappeared. A still better and more rapid method we find to be to catch the distillate in centrifuge tubes such as are used in urine analysis. The fine graduations allow of very accurate reading. Bulbs holding about 50 c.c. are blown on the tops of these tubes, and the modified tubes containing the xylol-water mixture whirled in a larger centrifuge than the one they were designed for. This obviates the necessity of waiting for the xylol to clear up. A complete moisture determination may be made in 45 minutes.

Absolute accuracy in the determination of water in the technical examination of lubricating greases is doubtless not important, though Holde has recently shown[2] the great influence exerted by even 1% of water on the drop point and the emulsified condition of lime-soap greases. Everyone who has driven off the water from a lime-soap

[1] A. L. Dean, "The Estimation of Moisture in Creosote Wood." Forest Service Circular, 134, Jan., 1906.
[2] Holde, "The Physical Condition of Solid Fats, and of Solutions of Calcium Soaps in Oil." Petroleum, 4, (I), 14, Oct. 7, 1908; Z. angew. Chem., 31, 2138–44 (1908); Chem., Abstr., 3, 1, 123 (1909).

grease containing a few hundredths of a per cent. of water has noticed the change from a buttery opaque mass to a gelatinous translucent one. Although not particularly important in the case of greases, the fact that the xylol method gives more accurate results than that of drying down is of importance in the analysis of other commercial products containing water.

13 commercial greases were analysed according to the methods given above, with the following results:

TABLE X.

No.	Name	Flash-point °	Consistency, grm., 20°	M. p., °	Per cent. calcium soap	Per cent. other thickeners
1	Graphite	195	18	93	11	16% graphite.
2	Summer motor..	160	170	87	38	....
3	Winter motor...	175	7	86	23	....
4	K 1...........	193	24	85	16	....
5	K 2...........	195	66	93	20	....
6	Auto..........	190	11	79	19	....
7	Tallow A[1]	210	150 (estimated)	52	......	1.4 potash soap.
8	Tallow XX[1]	215	200	49	......	2.1% potash soap. 30% paraffin.
9	Lead rosin oil...	240	7	102	......	1.75% lead.
10	Lime rosin oil...	198	31	77	......	9.9% CaO.
11	Lime rosin oil...	198	4	75	......	7.8% CaO.
12	Soda grease.....	215	35	83	......	22% sodium soap.
13	Non-fluid oil....	210	27	76	9.8	12.9% sodium soap.
14	No. 4 petrolatum	247	6	47	.....	....
15	Lard oil........	265	0	5	......	....

TABLE X.—Continued.

No.	Name	Per cent. H₂O	Per cent. saponifiable oil	Per cent. acids as oleic	Per cent. mineral oil
1	Graphite......................	Trace	17	0	56
2	Summer motor................	0.05	25	Trace	36.5
3	Winter motor.................	0.03	37[2]	6.1	40
4	K 1........................	0.2	16	0	67
5	K 2........................	0.3	20	0.3	60
6	Auto.......................	1.0	20	Trace	60
7	Tallow A[1]...................	2.5	73.5	0	22
8	Tallow XX[1]..................	Trace	48	0	20
9	Lead rosin...................	24.7	0	0	....
10	Lime rosin...................	Trace	0	0	....
11	Lime rosin...................	20.0	0	0	....
12	Soda grease..................	0.0	0	0	78[3]
13	Non-fluid oil.................	0	7	0	70.3
14	No. 4 petrolatum.............	0	0	0	100
15	Lard oil.....................	0	100	....	0

[1] Scented with nitrobenzol.
[2] Chiefly palm oil.
[3] Oil of 24.2° Be.

TABLE X.—Continued.

No.	Name	Maximum temperature of bearing above room temperature, °	Coefficient of friction at end of 3-hour run	Coefficient of friction, average throughout 3-hour run
1	Graphite	53	0.108	0.097
2	Summer motor	39	0.075	0.075
3	Winter motor	42	0.063	0.063
4	K 1	38	0.054	0.057
5	K 2	39	0.050	0.054
6	Auto	32	0.046	0.046
7	Tallow A	22	0.012	0.022
8	Tallow XX	25	0.018	0.029
9	Lead rosin	40	0.050	0.067
10	Lime rosin	42	0.017	0.048
11	Lime rosin	29	0.025	0.036
12	Soda grease	17	0.016	0.019
13	Non-fluid oil	25	0.016	0.026
14	No. 4 petrolatum	16	0.018	0.018
15	Lard oil	7	0.010	0.011

Friction tests were then made on these and on a petrolatum (Standard Oil, No. 4) and on a pure lard oil, as standards of reference.

The testing machine was a small Thurston, fitted with a compression grease cup, through which the grease was allowed to feed freely. The temperature was taken by a thermometer sunk in a small well, filled with oil in the upper brass. The Fahrenheit thermometer supplied with the instrument was not sufficiently delicate, and was replaced by a small centigrade one. The temperature of the bearing and the arc at which the pendulum stood, from which the coefficient of friction is figured, were noted at intervals of 1 minute for the first hour, and at every 5 or 10 minutes thereafter. The temperature of the room was taken periodically, and the r.p.m. noted.

The total pressure on the bearing in all cases was 240 pounds, equivalent to 60 pounds per square in. projected on the bearing. This was the highest pressure that could be obtained with the machine. It is probable that with a higher pressure the differences between the greases would be still more marked.

The speed was kept constant at 310–320 r.p.m. by a shunt-wound motor.

The general behaviour of a grease during the run was as follows: At first the coefficient of friction would be high, and the temperature would rise rapidly. In the case of a hard grease, as a rule, this would continue until the thermometer showed some certain temperature,

nearly up to the m. p. of the grease. The surface of the bearing probably did reach that temperature, although the thermometer did not register quite that temperature, as there was some chance for radiation.

After the grease had apparently melted, and the bearing was then in the state of an oil-lubricated bearing, the coefficient of friction would momentarily fall off, sometimes to a very low figure, and the temperature would drop rapidly. Then the grease would seem to stiffen again, and the coefficient and temperature would immediately rise. The graphite grease shows this behaviour to the greatest extent. This would go on for perhaps an hour, when a condition of equilibrium would be established, and a fairly constant reading would be attained. Many of these momentary fluctuations are smoothed out of the curves by taking averages of 5- or 10-minute periods and plotting these.

There is no direct proportionality between the results of the determination of any one analytical constant and the lubricating power, though there seems to be an approximate relation between the m. p. and the friction reducing power, as would be expected.

The relation, however, is not close enough to allow us to predict the lubricating value from the m. p. without taking the chemical composition and the physical constants into consideration.

The graphite grease showed an unexpectedly low lubricating power, and would be best fitted for a gear grease. The rosin oil greases, which are usually considered to be very poor lubricants, showed high friction at first, but after the bearing had warmed up enough to soften them somewhat, they compared well with the more expensive greases. The high moisture content of most of these greases would seem to be no drawback, but rather an advantage in rendering them less sticky.

VASELINE.

Petroleum Jelly. Petrolatum.

Vaseline consists of those portions of petroleum which are semi-solid or pasty at ordinary temperatures. It is taken from petroleum or ozokerite stills after the greater part of the oil has volatilised. The crystallisable paraffin is more or less removed, and the residue purified without distillation, treatment with sulphuric acid and superheated

steam and filtration through animal charcoal being the usual methods employed. An English patent was taken out in 1847 by C. B. Mansfield for a process for deodourising or decolourising petroleum sediment by means of animal charcoal.

Vaseline is now extensively used as a lubricant and to protect iron and steel goods from rust. It has been much used as a valuable basis for ointments. It varies somewhat in its physical characters according to its origin and quality. It is ordinarily a colourless or pale yellow, translucent, fluorescent semi-solid. The commoner kinds used for lubricating have a dark greenish or brownish colour. It is free from taste and smell. Under the microscope crystals are sometimes visible which become more numerous on cooling.

The commercial varieties may be classed under 2 heads: (1) those which, like the products from American petroleum, are obtained as a ready-formed mixture of hydrocarbons of gelatinous consistence; and (2) those made by directly mixing solid paraffin of low m. p. with heavy lubricating oil. The latter kind are less homogeneous and are liable to deposit crystals of paraffin on keeping, and hence are not so suited for the preparation of ointments as the American article.

Vaseline usually melts between 40° and 50°. At the b. p. of water, compared with water at 15.5°, the sp. gr. of vaseline ranges between 0.803 and 0.855, figures which present a striking contrast to those representing the sp. gr. of paraffin and ozokerite under the same circumstances (0.748 to 0.757). It is insoluble in water. Cold alcohol of 98% dissolves a small amount; in hot alcohol it dissolves freely to a clear solution, from which it separates in flakes on cooling.

Vaseline consists chiefly of paraffins, the iso-forms from $C_{16}H_{34}$ to $C_{20}H_{42}$ being apparently most abundant. A notable proportion of olefines is also present.

The following figures show the sp. gr. and bromine absorption of samples of vaseline and allied products examined in Allen's laboratory. The density determinations at 99° were made with a plummet and Westphal balance, and the bromine absorptions as in Vol. 2, page 26.

Description	Sp. gr.		Bromine absorption	
	Solid; at 15.5°	Melted; at 99°	Total	Br. as HBr
White pomade vaseline (Chesebrough Co.)	0.856	0.8036	11.3	1.8
Yellow vaseline (maker unknown)........	0.870	0.8140	1.1	0.0
Yellow vaseline (maker unknown)........	0.873	0.8172	7.2	1.1
White pomade ozokerine (J. C. & J. Field)	....	0.8110	1.1	0.3
Yellow pomade ozokerine (J. C. & J. Field)	0.909	0.8547	8.5	1.2
White cerasin mixture...................	....	0.8228	1.7	0.3
Petroleum jelly (Grindley & Co.)........	0.896	0.8421	2.9	0.7
Vaseline tallow........................	0.884	0.8374	10.2	1.7
Petrolina (Binghamton Oil Co.)..........	....	0.8145	7.9	1.3

In warm ether American vaseline dissolves freely to a clear solution exhibiting a strong blue fluorescence, and the liquid remains clear or becomes at most only slightly turbid on cooling. German vaseline, on the contrary, is said to form a thick solution and give a considerable deposit on cooling. Russian vaseline is stated to dissolve completely in warm ether, and give a clear solution which becomes turbid on cooling.

Vaseline is readily soluble in chloroform, benzene, carbon disulphide, and turpentine. From these and its ethereal solution alcohol precipitates it. Vaseline is miscible in all proportions with fixed and volatile oils. With glycerol it forms an intimate mixture which separates into its constituents when warmed, the melted vaseline floating on the glycerol. Treatment with water also removes the glycerol.

Vaseline is neutral in reaction, and but little affected by chemical reagents. It is not saponified or otherwise acted on by alkalies, and is unaffected by hydrochloric or dilute nitric acid. Boiling sulphuric acid of 1.60 and boiling nitric acid of 1.18 sp. gr. are said not to alter it; but fuming nitric acid colours it yellowish-red and sulphuric acid of 1.820 sp. gr. greyish-black, the acid itself acquiring a yellowish-brown colour. Some samples blacken on treatment with cold concentrated sulphuric acid, a reaction which indicates the presence of bodies other than paraffins. It does not oxidise or turn rancid on exposure to air. Vaseline intended for pharmaceutic use should be refined with the aid of acid.

Good vaseline should be completely volatile when heated in platinum, without giving any smell of burning fat (acrolein) or rosin. When agitated with twice its measure of strong alcohol it should remain practically undissolved. The spirit should not acquire an acid

or alkaline reaction, and should not give any noticeable precipitate on dilution with water. When agitated with cold cencentrated sulphuric acid diluted with 1/9 of its weight of water, vaseline gives no marked increase of temperature, and ought not to become very strongly coloured. When subjected to the saponification process employed for the determination of hydrocarbons in fixed oils, vaseline should yield to the ether an amount of unsaponifiable matter almost equal to the original weight of vaseline used for the experiment; while, on the other hand, the aqueous liquid separated from the ethereal layer should yield no notable precipitate on being acidified.

The United States Pharmacopœia has introduced, under the titles "Petrolatum" and "Petrolatum Liquidum," preparations equivalent to vaseline. They are defined as follows in the current (1900) issue:

PETROLATUM.

A mixture of hydrocarbons, chiefly of the methane series, obtained by distilling off the lighter and more volatile portions from petroleum, and purifying the residue.

An unctuous mass of about the consistence of an ointment, varying in colour from yellowish to light amber, having not more than a slight fluorescence, even after being melted, transparent in thin layers, completely amorphous; without odour or taste, but giving off, when heated, a faint petroleum-like odour.

If a portion of petrolatum be liquefied and brought to a temperature of 60° (140° F.), it should have a sp. gr. of from 0.820 to 0.850.

Petrolatum is insoluble in water; scarcely soluble in cold or hot alcohol or in cold absolute alcohol, but soluble in boiling absolute alcohol, and readily soluble in ether, chloroform, carbon bisulphide, oil of turpentine, petroleum benzin, benzene, and fixed or volatile oils.

The m. p. of petrolatum ranges between 45° and 48° (113° and 118.4° F.). If heated on a platinum foil to a still higher temperature, petrolatum should be completely volatilised without emitting any acrid odour.

If melted petrolatum be well shaken with water the latter should not redden blue litmus-paper.

If 10 grm. of petrolatum be digested at 100° (212° F.) for half an hour with 10 grm. of sodium hydroxide and 50 c.c. of water, the aqueous layer separated and supersaturated with sulphuric acid, no oily or solid

substance should separate (absence of fixed oils or fats of animal or vegetable origin and of rosin).

If 2 volumes of concentrated sulphuric acid be added to 1 volume of melted petrolatum in a test-tube placed in hot water, and the contents occasionally agitated during 15 minutes, the acid while acquiring a dark brown tint should not lose its transparency (limit of readily carbonisable organic impurities).

PETROLATUM LIQUIDUM.

Liquid Petrolatum.

A mixture of hydrocarbons, chiefly of the methane series, obtained by distilling off most of the lighter and more volatile portions from petroleum, and purifying the liquid residue.

A colourless or very slightly yellowish, oily, transparent liquid, without odour or taste, but giving off, when heated, a faint odour of petroleum.

Sp. gr. about 0.870 to 0.940 at 25° (77° F.).

If a test-tube be half-filled with liquid petrolatum and a piece of moistened blue litmus-paper be introduced, upon shaking the liquid vigorously the paper should not be reddened (absence of acid impurities).

In other respects liquid petrolatum has the characteristics of, and should respond to the tests given under, Petrolatum.

. The British Pharmacopœia (1905) recognizes "Paraffinum molle" and "Paraffinum liquidum." The former should melt at from 35.5° to 38.9°, have at its m. p. a sp. gr. of from 0.840 to 0.870, give off no unpleasant odour when heated to 48.9°, and be freely soluble in ether, chloroform, and benzene. The latter should boil at not below 360° and have a sp. gr. of from 0.885 to 0.890.

The German Pharmacopœia recognises "Paraffinum liquidum" and "Paraffinum solidum." The former should have a sp. gr. not less than 0.880 and should boil above 360°. The latter should melt at from 74° to 80°.

Mixtures of the intermediate members of the petroleum derivatives of such composition as to remain liquid at common temperatures and practically free from odour are now familiar commercial articles. One of these preparations is commercially known as "glycoline." Among the uses which may be made of it in the laboratory

is the preservation of specimens of sodium and potassium, which keep bright much longer in this liquid than in ordinary kerosene.

"Ozokerine," "fossiline," "chrysine," "cosmoline," "saxolene," "geoline," "petrolina," "vaseline tallow," etc., are trade-names of articles of the vaseline class.

PARAFFIN.

Paraffin Wax.   Solid Paraffin.

Paraffin is found native in the coal measures and other bituminous strata, constituting the minerals known as fossil wax, hatchettin, ozokerite, etc.   It exists also in solution in many kinds of petroleum, and is obtainable therefrom by distilling off the more volatile portions and exposing the remainder to a low temperature.   Solid paraffin may be obtained in a similar manner from the tars of wood, cannel coal, and bituminous shale, and is now manufactured on an enormous scale from the last source.   (See page 18.)

Paraffin is a white or bluish-white, waxy solid, without taste or smell. Its density and m. p. vary with its composition, and the same is true of its b. p., which is very high.   Exposure to continued heat, aided by pressure, resolves paraffin into liquid hydrocarbons, and the same result is partially obtained by distillation.   By merely raising the temperature to 370° it undergoes decomposition, with separation of carbon and formation of permanent gas, liquid products, and a paraffin of lower m. p.   It contains about 85% of carbon and 15% of hydrogen.

The sp. gr. of paraffin increases with its m. p., as is shown by the following results attained by Galletly from Boghead coal product:

Sp. gr.	M. p.	
0.8236	32.0° C.	89.6° F.
0.8480	39.0° C.	102.2° F.
0.8520	40.5° C.	104.9° F.
0.9090	[1]53.3° C.	128.0° F.
0.9110	[1]53.3° C.	128.0° F.
0.9243	58.0° C.	136.4° F.
0.9248	59.0° C.	138.2° F.
0.9400	80.0° C.	176.0° F.

G. Beilby (*J. Chem. Soc.*, **43,** 388) has given the following data respecting the sp. gr. of a sample of shale-oil paraffin melting at 38°.

[1] These temperatures are correctly quoted.

	Sp. gr.
In the solid state, at 21°..	0.8740
Dissolved in 0.885 paraffin oil, at 21°............................	0.7950
In the melted state (calculated to 21°.)	0.7956

From this it appears that paraffin in solution has practically the same density as when in the molten state. This result is comparable with one obtained by the author, who found that spirit of camphor has a volume equal to the sum of the volumes of the camphor and alcohol used in preparing it.

The data in the following table, obtained in Allen's laboratory, show the relations between the solidifying-point of paraffin wax and its density in the solid and liquid state. The determinations of sp. gr. of solid samples were in most cases made as described in Vol. 2, page 46, but, on repetition, the figures obtained were not very concordant. The density at 99° was determined by the plummet (Vol. 2, page 46), and the solidifying-point was ascertained by method d (Vol. 2, page 51).

Origin of sample	Sp. gr.		Solidifying-point,°
	Solid, at 15.5°	Liquid, at 99°	
1. Shale oil............................	0.8666	0.7481	44.0
2. Shale oil............................	0.8961	0.7494	47.0
3. Shale oil............................	0.9000	0.7517	52.0
4. Shale oil............................	0.9111	0.7572	58.5
5. American petroleum.................	0.9083	0.7535	53.8
6. Ozokerite..........................	....	0.7531	61.5
7. Rangoon tar........................	0.8831	0.7571	49.0

From these figures it appears that, except in the case of the refined ozokerite, there is a regular increase in the sp. gr. with a rise in the m. p., as was observed by Galletly. There is a striking contrast between the densities of the waxes in the molten state at 99° and the densities of the same samples when solid, the range in the latter case being, for the shale products, 5 times as great as in the former. In other words, the density of paraffin wax is far more constant when melted than in the solid state. It also appears that paraffin is much less dense in the

melted state than the oil from which it crystallises on cooling, a sample of which had a sp. gr. of 0.843 at 99°. Vaseline also is considerably denser than paraffin.

Paraffin melting from 32° to 43° exhibits a well-defined crystalline fracture; from 43° to 50° the crystals become much smaller and less marked, and from 50° upward the fracture is very close and fine in the grain. Paraffin that melts at 65° presents, on fracture, brilliant, white, acicular crystals having a silky lustre, and that melting at 77° closely resembles bleached beeswax, but the fracture is not conchoidal.

When paraffin is kept for some time under gentle pressure, the temperature being somewhat below its m. p., a molecular change occurs and the substance becomes transparent. A sudden change of temperature or a sharp blow or knock causes the mass to return to its original state, but it may be annealed by slow cooling.

Paraffin becomes plastic at a temperature considerably below its m. p., a fact which is disadvantageous when it is employed for making candles, but which is to a great extent obviated by a small admixture of stearic acid, wax, or other foreign body.

Mixtures of paraffins of different fusing-points melt at a temperature which is the mean of the m. p. of the constituent hydrocarbons; but the products obtained by melting together paraffin wax and stearic or palmitic acid, beeswax, etc., always have a m. p. *lower* than the mean of those of their constituents. This is well shown by the following table from Vincent's *Manufacturing Chemistry*, the results recorded being obtained from mixtures of the Musselburgh Company's stearic acid, melting at 130° F., with various proportions of 3 varieties of Young's paraffin:

Stearic acid	Paraffin	M. p. of mixture. Paraffin melting at		
		48.8°	52.2°	52.7°
55	45	45.5	45.3	46.4
60	40	48.3	46.6	47.7
65	35	49.4	47.7	48.8
70	30	50.3	50.3	50.3
75	25	51.4	51.1	51.1
80	20	52.0	52.0	52.0
85	15	52.2	52.7	52.7
90	10	53	53.3	54.1
95	5	53.6	53.8	54.4

When 2 pieces of paraffin are sharply struck together, a metallic ring is heard, the sound being sharper the higher the m. p. of the paraffin.

Paraffin is completely insoluble both in hot and cold water. It is insoluble in rectified spirit, and but sparingly soluble in boiling absolute alcohol, the dissolved portion separating again on cooling. It is moderately soluble in petroleum spirit, shale naphtha, kerosene, ether and benzene, essential oils, and fixed oils. It is rather more soluble in toluene than benzene, and in xylene than in toluene. Hence it is miscible with all kinds of vegetable and animal oils and fats. It differs from these in its indifference to alkalies, and cannot be saponified. If, however, the soap be made from a mixture containing carnauba wax as well as paraffin, the latter is completely dissolved by the alkali, a fact which is said to be attributable to its solubility in the myricyl alcohol, $C_{30}H_{61}OH$, which is a constituent of the carnauba wax.

Paraffin burns with a very bright but not smoky flame, and hence is much employed for making candles and tapers. *Paraffin candles* usually contain from 5 to 15% of stearic acid. The presence of the admixture may be detected by adding a little powdered fuchsine to the sample and keeping it at 100° for some time. If pure, the melted paraffin will remain uncoloured, but with 2% of stearic acid a pink colour is produced, and if as much as 5% be present, the whole mass becomes crimson. Coloured candles are made by dissolving the fuchsine or other colouring matter in stearic acid or beeswax, and adding the product to the paraffin until the desired tint is obtained.

Boiled with concentrated nitric acid, paraffin is oxidised, with formation of various products, of which the most characteristic are succinic acid, $C_4H_6O_5$, and cerotic acid, $C_{27}H_{54}O_2$, the production of the latter of which points to the presence of the hydrocarbon, $C_{27}H_{56}$, in the original substance. Cerotic acid was also the chief product obtained by Gill and Meusel by the oxidation of a paraffin, melting at 56°, by means of chromic acid mixture.

Paraffin is also violently oxidised by permanganate of potassium mixed with sulphuric acid and heated. Concentrated sulphuric acid attacks it at high temperatures, and the more readily the higher the m. p. of the sample.

When heated with sulphur, paraffin is decomposed, with evolution of hydrogen sulphide and separation of carbon.

Other chemical characteristics of paraffin and methods for separating it from *hydrocarbons* of other series are given on page 3 *et seq.*

For the quantitative analysis of mixtures of paraffin with *fatty acids* or *fats*, the process described in Vol 2, page 183, is suitable. The detection and estimation of paraffin in *beeswax* can be effected as described in Vol. 2, pages 249 and 258.

Paraffin Scale. *Crude Paraffin.*—"Scale" is the technical name for the crude paraffin deposited by cooling the oils holding it in solution. The lower the temperature employed for refrigeration, the lower the m. p. of the paraffin deposited.

In the practical assay of paraffin scale, methods must be employed which are acceptable under reasonable conditions by all interested parties. The following are the methods adopted by the Scottish Mineral Oil Association and certain representative purchasers:[1]

Sampling.—The sample is to be taken by means of a metal tube, which is made slightly conical; the small end is inserted in the scale, and by means of a handle, which is removable, it is forced through the scale to be sampled. By this means a cylindrical core of paraffin is obtained.

Care must be taken to see that the tube is of such a length that the sample will represent the whole length or depth of the cask, wagon, or bing.

Preservation of Samples.—Immediately after the sample has been drawn, it is to be thoroughly mixed, placed in suitable wide-mouthed bottles, which may be closed either with glass stoppers or good corks; if the latter are used, they should be covered with paraffin paper or soaked in melted paraffin wax before being inserted. The bottles are then finally sealed in the usual manner. The scale should be tightly packed into the bottles, which should be completely filled.

Estimation of Oil. (*a*) *Press.*—No special form of press is recommended for general adoption, but it must have some arrangement for indicating the pressure applied. The cup in which the scale is placed during the application of pressure should have an area of 20 sq. in.

(*b*) *Preparation of Sample.*—A quantity of the scale, after having been freed from water and dirt by melting and subsidence, is to be allowed to cool overnight to a temperature of 15.5°. The solid mass is then ground to a fine powder, a portion of which is used in the determination of the oil.

(*c*) *Quantity and Conditions.*—The quantity of scale to be used in the estimation of oil is to be 250 grains, which may, however, be

[1] *J. Soc. Chem. Ind.*, 1891, 342.

reduced to 150 grains in the event of the scale containing much oil (over 7%). With "soft" scale the smaller quantity should be taken.

(d) The temperature of the scale and the press is to be 15.5°.

(e) The scale is to remain under pressure for 15 minutes.

(f) Fine linen pressing cloths and a number of layers of filter-paper sufficient to absorb all the oil are to be used. The exterior papers must not be soiled by oil.

(g) The maximum pressure is to be 10 cwt. per sq. in., and the working pressure 9 cwt. per sq. in.

Estimation of Water.—The amount of water present in paraffin-scale may be estimated by either of the following processes:

(a) *Distillation from a Copper Flask.*—From 1 to 2 pounds of the scale are heated in a conical copper flask of about the following dimensions: 27.5 cm. (11 in.) high over all, 20 cm. (8 in.) diameter at the base, and 0.4 cm. (1.5 in.) at the neck. The bottom of the flask is slightly concave downward. This is connected to an ordinary Liebig condenser. By means of a powerful Bunsen burner or lamp the water, accompanied by a small quantity of light oil, is volatilised and condensed. The distillate is received in a narrow graduated measure, so that the volume of water can be readily ascertained. As a little water usually adheres to the sides of the condenser tube, this is to be washed out with hydrated gasolene or naphtha and added to the principal quantity.

(b) *Price's Company's Method.*—500 grains of the scale to be tested are weighed in a tared porcelain basin and heated with constant stirring to 110°, until bubbles cease to be given off; the loss is then determined.

500 grains of the *same scale*, which has been freed of its water and dirt by melting at a gentle heat and subsidence, are to be heated in the same way to a similar temperature for the same time, and the loss again determined. The loss in the second instance is now to be deducted from the loss found in the first experiment; the remainder is taken as the quantity of water present.

Determination of Dirt.—The amount of dirt present in scale is to be determined by melting a weighed quantity of the scale, and, after subsidence, pouring off the clear paraffin. The residue is then mixed with naphtha, thrown on a weighed dry filter-paper, washed with naphtha or gasolene, dried, and weighed. When available, the quantity of scale to be used in the estimation of the percentage of dirt should not be less than 1 pound.

Calculation of Results.—As the oil is determined on scale which has been freed from water and dirt, the result must be calculated back to the original scale containing water and dirt.

Determination of the Melting (Setting) Point of Solid Paraffin. —This may be determined by what is known as the "English" test; *i. e.*, a test-tube about 1 in. in diameter is filled to the depth of about 2 in. with the melted paraffin, a small thermometer is inserted, and the whole steadily stirred, while the test-tube and its contents are allowed to cool slowly. The temperature at which the thermometer remains stationary for a short time is the melting (setting) point.

What is technically known in England as the "m. p." of paraffin scale is in reality the solidifying-point, and can be ascertained by Dalican's method, Vol. 2, page 55.

Boverton Redwood (*J. Soc. Chem. Ind.*, 1884, **3**, 430) has devised a special machine for testing paraffin scale, and the greater part of that imported from America is sold on the results of the assay by Redwood's test. The apparatus consists of a press furnished with a gauge for indicating the pressure applied. The test is, of course, a purely arbitrary one, depending upon (*a*) temperature, (*b*) amount of pressure applied, (*c*) length of time during which the pressure is continued, and (*d*) quantity of scale operated upon in relation to the diameter of the press-cake. The operation is conducted at 15.5, which temperature must be closely adhered to. The quantity of scale operated upon is 500 grains, and the pressure is applied for 5 minutes. The gauge of the press indicates from 1 to 10 tons, and the working pressure is 9 tons on the whole surface of the press cake of 5 5/8 in. diameter, equal to about 7 cwt. per square in. The sample is placed between 2 circular pieces of filter-cloth in a turned iron cup into which the ram of the press fits, and a sufficient number of circular pieces of filtering paper are placed above and beneath the cloth to absorb the expressed oil. The press cake is carefully removed from the cloth at the expiration of 5 minutes, and the loss in weight noted. The proportion of oil in American scale usually ranges between 1 and 12%. Much depends upon the proper drawing and averaging of the samples of scale. A good plan is to sample one cask in 20 by taking out a core with a sampling iron driven into the centre of the cask, and then mix the sample by passing it through a small hand sausage-machine.

In America the paraffin scale is melted over a water-bath in a

hemispherical tinned iron or glass dish, 3 or 4 in. in diameter. The dish is then placed on a stand where slow cooling can take place, in a room at a temperature of about 15.5°, and a thermometer, with a spherical bulb 1/2 in. in diameter, is suspended over the centre of the dish so that 7/8 of the bulb is immersed in the paraffin. The surface of the melted scale is then carefully watched, and the temperature noted at which a "spider" extends from the edge of the liquid to the bulb of the thermometer. The "spider" or network makes its appearance before there is any uniform film over the surface, and is not readily observable unless the observer be suitably placed in relation to the source of light. Redwood, to whose published papers and private communications Allen was indebted for much information on the subject of petroleum-products, states that the results of the American test are from 2.5° to 3.0° F. higher than those obtained by the English test.

According to Lewkowitsch (*Chem. Anal. Oils, Fats, and Waxes*, 762), the German method of determining the solidifying point of paraffin-scale is as follows: A small beaker, 7 cm. high and 4 cm. in diameter, is filled with water and warmed to about 70°. A piece of the sample large enough to form a globule 6 mm. in diameter is dropped on the water. A standard thermometer is immersed in the water so that its bulb is entirely submerged and liquid allowed to cool slowly. The temperature at which a film is noticed on the paraffin globule is taken as the solidifying-point.

The following methods are improvements over the English method:

The solidifying-point is best determined by the method of Shukoff. 30–40 grm. of the paraffin is melted in a narrow flask inserted by means of a rubber stopper in a bottle, the same as is used for the solidifying-points of fats. (See Vol. 2, page 57.)

As soon as the temperature of the mass stated has dropped to about 5° above the solidifying point, the apparatus is strongly and regularly shaken until the contents is distinctly turbid. Then, without further shaking, one observes the point at which the thermometer remains constant and then rises. The highest point then reached is the solidifying-point of the paraffin.

Dr. Rich Kissling (*Rev. Fett. Harz. Ind.*, **15**, 46–9) modifies the method slightly by suggesting the use of a Dewar bulb, which is filled with melted paraffin to within 10 mm. of the upper edge. It is then suspended in a water-bath, the temperature of which is about 5°

above the solidifying-point of the sample. When the temperature of the bulb and the bath are the same, the bulb is shaken until the paraffin foams, when it is allowed to rest. This paraffin is still clear but close to the point of turbidity. The temperature is read from the thermometer in the bulb until it remains constant from 3 to 6 minutes.

True Paraffin.—Paraffin stock is tested for its content of true paraffin scale, according to Holde, as follows: 0.5 to 1.0 grm. of the substance is dissolved in a wide test-tube in ethyl ether, avoiding an excess of ether. A volume of absolute alcohol, equal to the ether used is added and filtered by means of suction in a funnel surrounded by a freezing mixture of ice and salt at a temperature of -20 to $-21°$. It is washed with a mixture of equal volumes of ether and absolute alcohol chilled likewise by immersion in a freezing mixture. After washing the paraffin is dissolved with hot benzol into a weighed flask and the paraffin estimated by weighing after the evaporation of the benzol.

PETROLEUM RESIDUUM.

In some works the distillation of petroleum is carried to actual coking and in others so far as to produce a kind of pitch. In other cases the process is stopped at an earlier stage, and the "petroleum residuum" obtained is separately treated.

Besides paraffins and olefines, the residues from American petroleum contain notable quantities of cyclic hydrocarbons, among which anthracene, phenanthrene, chrysene, chrysogene, and pyrene have been recognised, as also a hydrocarbon called thallene. From the residue from California petroleum the hydrocarbon picene, $C_{22}H_{14}$, has been isolated. When treated with strong sulphuric acid it yields a sulphonic acid, which dissolves in water with fine blue-green fluorescence.

For the assay of petroleum residues a method may be used similar to that employed for the examination of crude shale oil (page 16). That is, 500 c.c. should be distilled, the distillate washed with acid and sodium hydroxide, and the purified product again distilled, when it will yield *burning oil*, heavy oil containing paraffin, and "grease" which should be separately cooled and pressed. The oil separated from the *scale* is again treated with acid and soda, when it forms *finished lubricating oil*. A sample of residue examined by R. Tervet yielded: burning oil, 5.5%; lubricating oil, 50.6%; and paraffin scale, 5.8%.

Petroleum residues often contain a considerable proportion of

water, which cannot be separated by simply heating the substance. The residue should be treated with a large excess of petroleum spirit and the water allowed to settle out, any *gritty matter* being separated by filtration. In the United States petroleum residuum is largely used in the preparation of asphalt-paving mixtures.

CYCLIC HYDROCARBONS FROM COAL-TAR.

The tar obtained as a by-product in the manufacture of illuminating gas from bituminous coal was at one time a source of much annoyance to the gas-engineer, since no convenient disposition or use of it could be made. At the present day, however, it constitutes a valuable material, chiefly owing to the fact that it is rich in cyclic hydrocarbons, from which a long line of synthetic products of great practical value may be produced. Russian petroleum residuum has also been used as a source of cyclic hydrocarbons, but the present indications are that the utilization of the by-products of coke-ovens will afford the most economic and abundant supply of these bodies.

Tars from various kinds of coal, and even from the same kind under varying methods of operating, will obviously differ in composition, but will always be mixtures of many more or less analogous bodies. Modern methods of distillation at high temperatures result in changes of the composition of the coal-tar from what it was in the small retorts. Less open-chain hydrocarbons are found; in many cases only traces. Nearly all the constituents are of the aromatic series. A synopsis of the more important of these is given on page 198. The preliminary step in the separation of the different constituents is by fractional distillation. The table on page 198 shows the general character of this distribution as ordinarily carried out; more detailed information is given in connection with the description of the characteristic and important ingredients in each fraction.

In the United States a very large proportion of the illuminating gas is made from water-gas (carburetted water-gas), and the high temperature to which this gas is subjected in the "checker work" produces almost exclusively aromatic hydrocarbons.

The most important constituents of coal-tar may, from the standpoint of the analyst, be arranged in 4 groups, as derivatives of *Benzene*, *Naphthalene*, *Anthracene*, and *Pitch*. Each of the first named forms the starting-point of a homologous series, and of an extensive and complex series of derivatives.

COMPOSITION OF THE PRINCIPAL FRACTIONS OF COAL-TAR.

Crude naphtha. Light oils.	Dead oils. Creosote oils.	Green or Anthracene oils.	Pitch.
(Sp. gr. less than 1.000.) Distilling below 180°. Methanes (paraffins). Tetrane to decane. Ethenes (olefines). Pentene to heptene. Ethines (acetylenes). Benzenes. Benzene to durene. Benzene hexhydrides. Naphthalene hydrides. Phenol (carbolic acid). Methylphenols (cresols). Pyridines. Sulphur compounds (thiophenes). Amine derivatives.	(Sp. gr. more than 1.000.) Distilling between 180° and 270°. Phenol. Methylphenols (cresols). Naphthalenes. Naphthalene hydrides. Methyl-naphthalenes. Diphenyl. Anilines. Leucolines, Pyridines. Quinolines.	Distilling above 270°. Acenaphthene. Fluorene. Phenanthrene. Retene. Anthracene. Pyrene. Chrysene. Picene. Benzerythrene. Solid paraffin. Benzonitrile. Carbazol. Acridine.	

BENZENE AND DERIVATIVES.

The following is a synopsis of the empirical and rational formulæ, conventional and systematic names of some of the known members of the series. Isomerism does not occur in the first two forms:

Empirical formula	Rational formula	Conventional name	Systematic name
C_6H_6		Benzene	
C_7H_8	$C_6H_5CH_3$	Toluene.	Methylbenzene.
C_8H_{10}	$C_6H_5C_2H_5$	. . . .	Ethylbenzene.
	$C_6H_4(CH_3)_2$	Xylenes	Dimethylbenzenes.
C_9H_{12}	$C_6H_3(CH_3)_3$	Mesitylene . . . . ⎫	
		Pseudocumene . . . . ⎬	Trimethylbenzenes.
		Hemimellithene . . . ⎭	
	$C_6H_5C_3H_7$	Cumene	Isopropylbenzene.
$C_{10}H_{14}$	$C_6H_2(CH_3)_4$	Durene . . . . ⎫	
		Isodurene . . . . ⎬	Tetramethylbenzenes
		Prehnitene . . . . ⎭	
	$C_6H_4(CH_3)(C_3H_7)$	Cymene	Methylisopropylben-zene.
$C_{11}H_{16}$	$C_6H(CH_3)_5$	. . . .	Pentamethylbenzene.
$C_{12}H_{18}$	$C_6(CH_3)_6$	. . . .	Hexamethylbenzene.

The homologues of benzene prominently occurring in coal-tar are bodies in which 1 or more of the atoms of hydrogen of benzene are replaced by methyl, CH_3. Meta-derivatives are more abundant than either ortho- or para-derivatives. Higher homologues than tetramethylbenzene are rare, if occurring at all.

The members of the benzene series present very close resemblances both in their physical and chemical characters, and hence, with the exceptions specified below, the description given of benzene may be regarded as of general applicability to the others.

Benzene, C_6H_6.—This substance was discovered by Faraday in the liquid obtained by compressing coal-gas, and subsequently prepared by Mitscherlich by distilling calcium benzoate. Mansfield, a pupil of A. W. Hofmann, first obtained benzene in practical quantity from coal-tar. He lost his life by an accident that occurred while preparing a sample for exhibition at the Paris Exposition of 1854. The chemistry of benzene has become of immense importance, and research has been materially aided by the general acceptance of Kekulé's theory of the benzene-ring; namely, that the carbon atoms are arranged in a closed

chain, so that 6 valencies are latent, 12 are concerned in forming the chain, and the remaining 6 are saturated by the hydrogen. Various suggestions have been made as to the distribution of the latent valencies, but the subject does not need elaborate consideration here. The play of affinities cannot be shown without the use of stereochemical formulæ. For convenience the benzene molecule is represented by a hexagon, which, if unmodified, stands for C_6H_6. When any sign is attached without a connecting line to any angle of the hexagon, it indicates that the body represented is substituted for the hydrogen at that point. To assist in the nomenclature of the benzene derivatives the hexagon is "oriented"—that is, the angles are numbered, the figures 1 to 6 being used, arranged in the direction of the figures of a clock.

Orientation.   Nitrobenzene.   Hydroxybenzene.   Amidobenzene.
Mono-substitution Compounds.
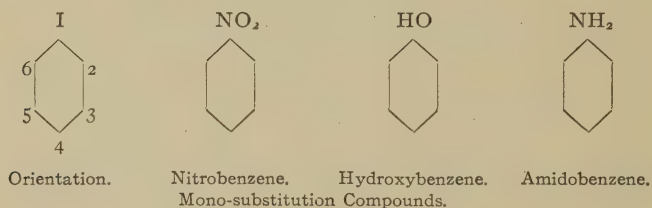
When only 1 hydrogen atom is replaced in a given molecule, the position is unimportant; but when more than 1 is replaced, isomeric forms are always produced. Many of these have been obtained. When 2 hydrogen atoms are replaced by the same or different radicles, 3 isomeric forms are possible. Representing the substituting radicles by X, the following formulæ will show the forms; and names:

1-2 (ortho)   1-3 (meta)   1-4 (para)
Di-substitution Compounds.
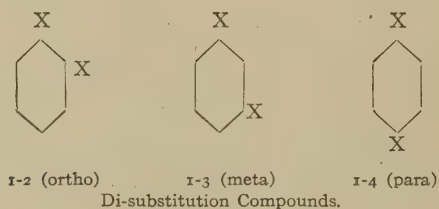
The numerical system 1-2, 1-3, 1-4 is to be preferred to that by prefixes, as the latter becomes complicated and difficult to understand with the complex derivatives. The replacement of three

hydrogen atoms by the same substances also gives rise to three forms; thus:
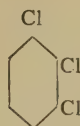
| 1-2-3 | 1-2-4 | 1-3-5 |
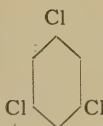
Trichlorbenzenes.

These tri-substitution compounds have been called, respectively, *conseculive* or *adjacent, asymmetrical,* and *symmetrical.*

When 3 hydrogen atoms are substituted by *different* radicles the number of possible isomeric forms is much increased. Further details will be given in connection with the description of special substances.

The additive compounds are formed not only with chlorine and bromine, but also with hydrogen. Benzene hexhydride, $C_6H_6H_6$, is isomeric with hexene. The following table shows the sp. gr. and b. p. of some of the hexhydrides:

Formula	B. p., °	Sp. gr.		
C_6H_{12}	69	0.760 at 0°	—	Compared
C_7H_{14}	97	0.772 at 0°	0.758 at 20°	with
C_8H_{16}	118	0.781 at 0°	0.765 at 20°	water
C_9H_{18}	135–138	0.790 (?) at 0°	—	at 0°
$C_{10}H_{20}$	153–158	0.802 at 0°	0.788 at 23°	

The members of this series are known as naphthenes. The naphthenes behave in many respects like saturated hydrocarbons, being incapable of forming additive compounds, offering great resistance to the action of oxidising agents, and, when yielding, splitting up completely, with formation of carbon dioxide and water as the chief products. They are not acted on in the cold by bromine, fuming sulphuric acid, nor nitric acid of sp. gr. 1.4; but fuming nitric acid, or a mixture of nitric and sulphuric acids, converts them into the nitro-derivatives of the benzene hydrocarbons. Naphthenes have been found largely in Caucasian petroleum, and are present also in American petroleum (see pages 41 and 42).

The light oil from coal-tar, known as commercial "benzol," con-
sists chiefly of a mixture of benzene and its homologues in variable
proportions. The method of assay is described on page 206 *et seq*.
The characters of benzene and its immediate homologues are de-
scribed in separate sections.

The term benzol is one frequently applied to the hydrocarbon
benzene, but when used at all it should be strictly limited in its applica-
tion to the mixture of homologous hydrocarbons obtained from light
coal-tar oil, of which benzene, C_6H_6, is the most important constituent.
The technical product is generally known as benzol.

Benzene is produced by a great number of reactions, and also
results from the heating of various hydrocarbons and other organic
bodies. It occurs in certain petroleums.

In practice, benzene is obtained from the portion of coal-tar which
distils below 100°, technically known as "light oils." To prepare pure
benzene, the oil is agitated successively with dilute sulphuric acid,
water, and milk of lime or caustic soda solution. It is next digested,
at 100°, with 5% by volume of concentrated sulphuric acid for several
hours, in order to separate thiophene and the hydrocarbons of the ole-
fine and acetylene series, and this treatment is continued as long as fresh
quantities of acid continue to be blackened by it. The purified product
is then separated and fractionally distilled, the portion which passes
over below 90° being collected separately. This is cooled by a freezing
mixture, when the benzene crystallises out, and is separated from the
more fusible hydrocarbons by draining on a vacuum-filter. If a pure
product be required, the benzene is melted and recrystallised several
times, the mother-liquor being separated as before.

Pure benzene is a colourless, very limpid, highly refractive liquid,
of a peculiar and somewhat agreeable odour. When subjected to a
freezing mixture it solidifies to a brilliant white mass of fern-like
tufts, which melts at 5.5°, and boils without decomposition at 80.5°,
emitting a highly inflammable vapour, which burns with a luminous and
very smoky flame. Benzene is practically insoluble in, though com-
municating its odour to, water, but is miscible (apparently in all pro-
portions) with methyl, ethyl, and amyl alcohols, ether, chloroform,
carbon tetrachloride, petroleum spirit, turpentine, absolute phenol,
and fixed and volatile oils.

Hot benzene dissolves sulphur, phosphorus, and iodine. It is an
excellent solvent for gutta-percha and india-rubber, and which are

left unaltered on evaporation. It also dissolves waxes, fats, and fatty acids.

The following are determinations of the sp. gr. of benzene:

Source of benzene	Density	Temperature,°	Observer
....	0.8991	0	Kopp.
....	0.8957	0	Warren.
....	0.8820	15	Warren.
Benzoic acid..................	0.9002	0	Adrieenz.
Benzoic acid..................	0.8846	15	Adrieenz.
Benzoic acid..................	0.8689	30	Adrieenz.
Benzoic acid..................	0.8133	80	Adrieenz.
Coal-tar......................	0.9012	0	Adrieenz.
Coal-tar......................	0.8850	15	Nickels.

Benzene may be heated to 400° in a sealed tube without change; but when passed through a tube heated to a bright redness it yields hydrogen, together with diphenyl, $C_{12}H_{10}$, and other hydrocarbons. Benzene is not acted on by distilling it with metallic sodium. Alkali hydroxides have no effect on it. It dissolves entirely when heated to 100° for some hours with 4 or 5 times its volume of concentrated sulphuric acid. The resulting liquid contains benzenesulphonic acid, $C_6H_5SO_3H$, and is colourless if pure benzene be employed. At very high temperatures, or when fuming sulphuric acid is employed, benzenedisulphonic acids are produced. Under the influence of oxidising agents benzene yields a number of interesting products, according to the treatment to which it is subjected. Thus:

a. By the action of chromic oxychloride on a solution of benzene in glacial acetic acid, trichloroquinone, $C_6HCl_3O_2$, is formed.

b. By the action of manganese dioxide and concentrated sulphuric acid, benzene yields carbon dioxide, formic acid, and water, together with small quantities of benzoic, phthalic, and terephthalic acids.

c. By the action of concentrated nitric acid, benzene is readily converted into nitrobenzene, $C_6H_5NO_2$; and by the continued action of the acid, especially if hot or mixed with sulphuric acid, dinitrobenzenes $C_6H_4(NO_2)_2$, are produced.

By the action of chlorine or bromine in the dark or diffused light, benzene is converted into chlorinated or brominated derivatives, in some cases 5 out of the 6 atoms of hydrogen being replaced. In direct sunlight, chlorine and bromine form additive compounds with

benzene, of which benzene hexachloride, $C_6H_6Cl_6$, is a type. Iodine alone has no action on benzene, but when a mixture of benzene with iodine and iodic acid is heated iodobenzenes are formed.

By prolonged treatment with hydriodic acid, under high pressure, benzene is converted into benzene hexhydride, C_6H_{12}, a substance isomeric with hexene.

Separation and Recognition of Benzene.—When in a pure state and in tolerable quantity, benzene is readily recognisable by its smell, sp. gr., and b. p. The chemical tests capable of ready application are few, the most satisfactory being the formation of nitrobenzene with nitric acid, followed by the action of reducing agents on the nitro-compound, and recognition of the aniline so formed.

This test is only applicable to benzene in approximate purity, or at least free from certain admixtures. With complex mixtures one or all of the following means must be adopted to separate the benzene from interfering bodies:

1. The liquid should be agitated with solution of sodium hydroxide, and separated from the aqueous layer. This treatment removes phenols and other bodies of an acid character.

2. The purified oily liquid should be separated from non-volatile matters by distillation in a small retort or flask furnished with a thermometer and good condensing arrangement. The portion passing over between 65° and 100° will contain any benzene which may be present, and should be collected separately and treated as follows:

3. The fraction passing over between 65° and 100° is shaken with a small quantity of cold concentrated sulphuric acid, and the treatment repeated, if necessary, with successive small portions of acid till no further blackening ensues. Thiophene and members of the olefine and acetylene series are thus removed. If at this point the liquid be warmed with excess of concentrated sulphuric acid, the acid liquid separated, heated to from 180° to 200° and a current of steam passed through it, all benzene and homologues which had dissolved as sulphonic acids will be recovered nearly pure.

4. The purified oil is separated from the acid and washed by agitation with dilute sodium hydroxide solution.

5. The product of the last operation should next be redistilled in an apparatus provided with a dephlegmator, and the fraction passing over between 78° and 84° collected separately, and, if thought desirable, again fractionated, the portion distilling between 80° and

82° being collected separately.   The product will consist of benzene, probably mixed with more or less of other bodies having approximately the same b. p., those most likely to be present being thiophen, carbon disulphide, toluene, and benzene hexhydride.

6. The first of these may be removed by treatment with aluminum chloride (see page 211), and the second by alcoholic potash (see page 226), while the remaining bodies may be further separated by again fractionally distilling, and remain liquid on exposure to 0° at which temperature benzene solidifies.

When present in but small proportion in a mixture of volatile bodies the foregoing process wholly fails to isolate the benzene present, and in many other cases it is unnecessary to obtain the hydrocarbon in a state of absolute purity in order to demonstrate its existence.   As a rule, it is sufficient to treat the partially purified substance resulting from process 4 for nitrobenzene as described below.

The benzene, having been concentrated and obtained more or less pure in the manner above described, is next treated with about twice its measure of fuming nitric acid of 1.50 sp. gr.   The operation is conducted in a small flask or retort furnished with an inverted condenser. If a vigorous action occurs, no extraneous heat need be applied; but if the reaction be sluggish, the liquid should be well agitated and moderately heated for a few minutes.   The flask is then cooled and the contents transferred to a tapped separator.   If separation into distinct strata occurs, *all except the top stratum*[1] are run off, while still warm, through the tap into a quantity of cold water.   If this liquid remain clear, no nitrobenzene has been formed, and consequently benzene was not present.   In presence of a considerable quantity of benzene, separation of yellow, oily nitrobenzene will occur at the bottom of the water, and a marked odour of bitter almonds will be perceived.   With smaller quantities, the nitrobenzene will form a finely divided precipitate, which will collect after some hours at the bottom of the vessel.   The liquid is passed through a wet filter, washed with cold water, and the nitrobenzene collected is dissolved by dropping alcohol on the filter. The alcoholic solution thus obtained is then treated with zinc and hydrochloric acid, in the manner described on page 212, and the resultant *aniline* detected by bleaching powder.

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[1] In the case of mixtures of petroleum spirit and benzene, 3 layers are formed, the uppermost consisting of unaltered paraffins, the middle one of nitrobenzene, and the lowest of a solution of nitrobenzene in nitric acid.   If the proportion of benzene in the mixture be moderate, the nitro-compound produced remains wholly in solution in the nitric acid until the latter is diluted.

For the estimation of benzene in complex mixtures, the only available method is to separate fixed matters, purify by treating with acid and alkali, as already described, then to remove any carbon disulphide by alcoholic potash (see page 226 *et seq.*), and subsequently to carefully fractionate the purified hydrocarbons in a bulb apparatus, as directed. The product may then be converted into nitrobenzene as described on page 211, the latter substance being dissolved in strong sulphuric acid and any residual hydrocarbons deducted from the apparent benzene previously found.

For the estimation of benzene and its homologues in the liquid obtained by compressing the gaseous hydrocarbons obtained by subjecting petroleum to a red heat, as in the Pintsch system of lighting railway carriages, C. G. Williams rejects the portion distilling below 65.5°, and treats the remainder with its own volume of commercial nitric acid, previously dilated with an equal volume of water. On distilling the mixture at 100°, the benzene and its homologues readily come over, while the olefines are converted into compounds, which remain in the still.

COMMERCIAL BENZENE (BENZOL).

The benzene of the English market varies in purity from an article containing only insignificant proportions of other bodies to the "90," "50," and "30"% benzols of the tar distiller. The composition and methods of assaying these products are described in a subsequent section (page 222 *et seq.*). Commercial benzol, when sold retail, is sometimes entirely replaced by petroleum spirit. Shale naphtha may also be substituted. These products are readily distinguished from the coal-tar products by the tests described on page 116.

Benzene is now manufactured in large quantities of such purity that from 95 to 98% will distil within 1° of the theoretical b. p. The assay of such products is conducted by more rigid methods than those employed for ordinary benzols. Thus, the distillation is conducted on 100 c.c., which is fractionated in a flask with side-tube, the bulb of the thermometer being adjusted so as to be just below the tubulure.

In some cases, and in conformity with Continental contracts, commercial benzene is subjected to the following special tests: (*a*) 1 c.c. of the sample is agitated with 20 c.c. of pure concentrated sulphuric

acid in a small stoppered bottle, and allowed to stand some hours. The colourisation at the end of this time should be very slight, never exceeding a pale straw-yellow. (b) 10 c.c. of it is agitated in a stoppered bottle with successive small quantities of saturated bromine-water, until a yellow tint is obtained, which persists for some minutes. Not more than 0.5 c.c. of bromine-water should be required to produce this result.

For the purpose of determining the available benzene in a mixture, G. Lunge ("Coal Tar and Ammonia," 3d English Ed., p. 626) recommends the *nitration test*, which depends on the production of nitrobenzene. He describes it as follows: 100 c.c. of the sample are placed in a 500 c.c. flask provided with a cork carrying 2 tubes. A mixture of 150 grm. of nitric acid (sp. gr. 1.4), and 180 to 200 grm. of sulphuric acid (sp. gr. 1.84) is prepared and allowed to cool. Portions of this mixture are placed in the stoppered tube and allowed to flow drop by drop into the benzene, shaking this up almost instantly. If the temperature rises, the flask must be cooled by immersion in water. When addition of acid ceases to produce rise of temperature, the flask should be heated gently for an hour or 2, during which time it will be an advantage to connect the second tube with a reflux condenser. Allow the mixture to settle, and separate the layers by a separatory funnel. Most of the crude nitrobenzene is in the upper layer. The lower (acid) layer should be diluted with several times its bulk of water and allowed to stand for a few hours. Any oily liquid separating should be added to the nitrobenzene. Wash the latter with water several times, then with a very dilute solution of sodium hydroxide, and once again with water. Care should be taken that none of the product is lost in these washings. The washed nitrobenzene is then allowed to settle, carefully separated, redistilled in a fractionating flask until a temperature of 150° is reached, and the distillate once more nitrated, using a large excess of the acid mixture. Any material remaining undissolved may be regarded as non-nitrable hydrocarbons. 157.6 parts of nitrobenzene correspond to 100 parts of benzene.

For testing crude benzene by fractional distillation the methods described on page 48 may be employed. The French Government has adopted a compact apparatus devised by Regnault, and consists in a cylindrical copper retort, of not less than 300 c.c. capacity, connected with a condenser. 5 glass receivers marked in c.c. are provided with means for quickly changing from one to another. 100 c.c. of the

sample are placed in the retort, and the thermometer fixed so that the bulb does not dip into the oil and the mark of 80° comes just above the cork. The receivers are changed at 100°, 120°, 140°, 160°, and 180°.

In the United States the usual commercial grades of benzol are "Benzol C. P." (crystallisable), "100%," "90%," "50%," and straw-coloured. The first mentioned is very nearly pure benzol and can be crystallised by chilling to 5°. The "100%" product should give 100% over at 100° on distillation; the "90%" 90% over at 100°, and the same "50%" 50% at 100°. The straw-coloured benzol is the same as the 90%, only unwashed.

The following is a list of the "benzols," etc., produced by the Barrett Manufacturing Co. at Philadelphia, Pa.:

Benzol C. P., water-white	Solvent naphtha, water-white
Benzol 100%, water-white	Benzol, straw-coloured
Benzol 90%, water-white	Toluol, straw-coloured
Benzol 50%, water-white	Barrettol
Toluol C. P., water-white	Heavy naphtha, dark
Toluol Commercial, water-white	Special heavy oil, free from naph-
Xylol, pure, water-white	thalene
Benzol 160°, water-white	Creosote oil, dark (deposits naphthalene)

(To Mr. Jayne, of the chemical department of this company, and their chemist, Mr. Weiss, is due the commercial methods of analysis of benzols, carbolic acids, given herewith and on page 307).

The following general tests are applied to water-white benzols:

Distillation Test.—In distilling benzols (products enumerated above) 100 c.c. distilling flasks are used, with side-tube delivery. They should be made of Jena glass as the distillations are pushed to dryness. To do this gauze must not be used, but the flasks rest in a hole in a piece of asbestos board and very small flames from extremely small Bunsen burners are used.

A burner found useful by the reviser of this edition consists of a tube 1 3/4 in. long with an opening at the top 1/4 in.; air mixes with the gas in the base of the burner. The flame must be protected from draughts by large pieces of asbestos or sheet metal, chimneys of tin or mica around the burner cause superheating of the vapours. Very carefully standardized thermometers are used for this work, but correction for exposed stem is not made. The distillation test is the most important test and serves to grade oil most readily.

Sulphuric Acid, or Wash Test.—This test is only applied to water-white oils, as it would mean nothing with unrefined oils. Pure concentrated sulphuric acid is shaken with 3 or 4 parts of the oil in small glass-stoppered bottles of clear colourless glass.

The purity of the oil is judged by the colour it gives to the acid. After vigorous shaking for about 1 minute the mixture is allowed to settle for 10 minutes before recording the test.

Sp. Gr.—This is best taken by means of a Westphal balance at 15°.

In the works it is customary to use specially made hydrometers, that are carefully standardised.

"Benzol C. P."—This grade should all boil over within 2° at about 80°, say from 80–82°. The sulphuric acid test should give acid almost uncoloured or very pale straw-colour, the benzol is absolutely uncoloured, as in the case of most water-white products. The sp. gr. should be 0.882–0.884. The following table shows the results of tests on these products.

	Distillation	Sp. gr.	Acid test
Benzol C. P	All over within 2° at about 80°.	0.882–0.884	Acid very pale straw.
Benzol 100%	All over at 100°, (flask dry).	0.880–0.882	Acid straw.
Benzol 90%	90% over at 100°, all over by 120°.	0.879–0.882	Acid slightly yellow.
Benzol 50%	50% over at 100°, all over at 120°–130°.	0.870–0.876	Acid yellow.
Toluol	Within 2 degrees around 100°.	0.870–0.872	Very pale straw.
Toluol, commercial ...	At least 90% at 120°; at least 95% at 130°; dry at 140°.	0.869–.0871	....
Pure xylol, commercial.	Should boil between limits 134–145°.	0.866–0.869	....
Solvent benzol 160 ...	90% over at 160°	0.866–0.870	Acid yellow.

Heavy tar oil supposed to be free from naphthalene. This may be tested by distillation in a 100 c.c. flask as used for benzols. Its gravity should be greater than that of water. On being surrounded by ice in a small test-tube and a small crystal of naphthalene added, no more naphthalene should be found other than that added.

Straw-coloured benzol shows distillation test and sp. gr. about the same as 90% benzol. Straw-coloured toluol the same as commercial toluol, as it is the unwashed product.

Barretol is a coal-tar distillate that has about the same evaporative power as turpentine; it is used for cleaning type, varnish stains, solvent for rubber, etc.

THIOPHEN, C_4H_4S.

This body is present to the extent of 0.5% or more in all commercial benzene prepared from coal-tar.

Pure thiophen is a colourless, mobile liquid, boiling at 84°, and having a density of 1.07 at 15°. It is not miscible with water, and is not attacked by alkalies or alkali metals. With concentrated sulphuric acid it forms a sulphonic acid, and is oxidised very rapidly by nitric acid. Mono- and dinitrothiophen have, however, been obtained and may be present in the best commercial nitrobenzols. Bromine forms monobromthiophen, boiling at 150° and having a density of 1.652 at 23°; or, if a larger quantity of bromine is used, forms dibromthiophen, $C_4H_2Br_2S$, which is a colourless liquid boiling at 211° and of 2.147 sp. gr. at 23°. In its reactions this body closely resembles thiophen.

Many of the colour-reactions of commercial benzene and toluene are really due to the presence of thiophen. This is true of the brown colour produced on agitation with strong sulphuric acid, and especially the reaction observed by Laubenheimer. To apply this test, a dilute solution of phenanthraquinone in glacial acetic acid is treated with a few drops of the liquid to be examined, the mixture well cooled, and concentrated sulphuric acid then added drop by drop, the resulting solution after a few minutes being treated with water. A colouring matter separates, which, on agitation with chloroform, dissolves to a fine green liquid. On shaking 2 c.c. of benzene with 0.5 c.c. of sulphuric acid and 1 drop of fuming nitric acid, a blue or green tint indicates the presence of thiophen. Another highly characteristic reaction is the deep blue indophenin produced on agitating thiophen with isatin and strong sulphuric acid. When the proportion of thiophen is large, a dirty brown is produced. If the mixture be warmed, the same reaction is produced by many of the derivatives of thiophen, including dibromthiophen, thiophen-sulphonic acid, $C_4H_3S.SO_3H$, and thiophenic acid, $C_4H_3S.COOH$. According to H. Kreis (*Chem. Zeit.*, **26,** 523, 1902), if benzene, containing even very minute amounts of thiophen, is shaken with a very dilute solution of thalline (*p*-methoxytetrahydroquinoline) and a little (1.42) nitric acid, the acid becomes coloured intensely violet. This reaction is delicate with a solution of thalline and thiophen in benzene as dilute as 1–100,000. The violet colouration is not permanent, it changes gradually to reddish and finally to yellow. The purple reaction of dinitrobenzene with

alcohol and potassium hydroxide is due to the presence of nitro- or dinitrothiophen.

For the removal of thiophen from benzene, Haller and Michel (*Bull. Soc. Chim.*, 1896, 1065) employ aluminum chloride. 1% is sufficient when the sample contains but little thiophen; but when the proportion is greater, 4 or 5% may be needed. The aluminum chloride is agitated with the benzene and then allowed to stand, when a viscous, reddish product collects at the bottom. The benzene may be distilled off at once or after separation from this liquid.

Estimation of Thiophen in Benzene (Denigès, *Bull. Soc. Chim.*, 1896, 1064).—2 c.c. of the sample are placed in a 60 c.c. stoppered flask with 30 c.c. of methyl alcohol, free from acetone, and 10 c.c of mercuric sulphate solution. The flask is closed and the mixture allowed to stand for about 20 minutes. An insoluble compound, $2HgO, HgSO_4, C_4H_4S$, is formed, and is removed by filtration. 21 c.c. of the filtrate (0.1 c.c. of the sample) are placed in a litre flask with 350 c.c. of water, 15 c.c. of ammonium hydroxide solution, 10 c.c. N/10 potassium cyanide solution, and 5 or 6 6 drops of a 20% solution of potassium iodide, and the whole well shaken. If not perfectly clear, a gentle heat may be applied, and then, after cooling, N/10 silver nitrate is added until a permanent turbidity results. The amount of thiophen (x) can be calculated by the formula:

$$x = 2.8 \, (n - 0.3) \, ;$$

in which n equals the number of c.c. silver nitrate solution used.

Methylthiophen or thiotoluene, C_5H_6S, is contained in impure toluene, from which it is isolated with difficulty as a colourless liquid boiling at 113° C. *Dimethylthiophen*, or *thioxene*, C_6H_8S, is also present in coal-tar naphtha.

NITROBENZENE, $C_6H_5NO_2$.

Nitrobenzene, called "nitrobenzol" commercially, is a product of the action of nitric acid on benzene, $C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O$. The acid should not be of lower sp. gr. than 1.45; on the large scale it is employed in admixture with sulphuric acid. Great heat is evolved, and more or less red fumes are produced. When the action is over, the product may be poured into water, when the nitrobenzene sinks to the bottom as a yellow oil.

Pure nitrobenzene is a pale yellow liquid, having an odour resembling that of the essential oil of bitter almonds or benzaldehyde, C_7H_6O, but differs from that body in many respects besides chemical composition. Its odour has led to its extensive use as a scenting and flavouring agent under the name of "Essence of Mirbane." It is nearly insoluble in water, but dissolves in nitric acid, being reprecipitated on dilution. It is soluble without alteration in sulphuric acid of 1.84 sp. gr. Fuming sulphuric acid converts it into m-nitrobenzol-sulphonic acid. The sp. gr. of nitrobenzene is 1.208 at 15° The m. p. after having been chilled to the solid state is 3°. The b. p. is 206–207°. Nitrobenzene is readily volatile with steam. 1 part of nitrobenzene distils with 6 parts of water at 1 atmosphere pressure. It is readily soluble in alcohol, and is miscible in all proportions with ether, benzene, and oils, and has great stability, being unaffected by chlorine or bromine even at the b. p., unless iodine or antimonic chloride be simultaneously present.

The vapour of nitrobenzene is distinctly coloured, closely resembling that of chlorine. This is easily visible in a depth of 5 cm., and is strongly marked in a depth of 10 cm. When light is transmitted through the vapour, no bands of absorption are produced in the visible spectrum. The violet and the blue are absorbed, but less strongly than with the fluid.

By treatment with a mixture of sulphuric acid and the strongest nitric acid, nitrobenzene is converted into a mixture of the three isomeric dinitrobenzenes, $C_6H_4(NO_2)_2$. These form pale yellow crystals.

Nitrobenzene is scarcely affected by aqueous alkalies, even when boiling, but is converted by alcoholic potash into a mixture of azobenzene, $(C_6H_5)_2N_2$, and azoxybenzene, $(C_6H_5N)_2O$.

Under the influence of reducing agents, e. g., hydrogen sulphide, zinc and hydrochloric acid, or acetic acid and iron filings, nitrobenzene is converted into aniline, $C_6H_5 \cdot H_2N$, the production of which affords one of the most delicate and characteristic tests for nitrobenzene. The alcoholic solution of the nitrobenzene should be mixed with hydrochloric acid and boiled for some time with metallic zinc. The liquid is next diluted, neutralised with sodium hydroxide, and a clear solution of bleaching powder cautiously added. A blue or purple colouration, often appearing somewhat slowly, and gradually changing to brown, will be produced if aniline, resulting from the reduction of

nitrobenzene, be present. According to Balls, magnesium ribbon, with the addition of a few drops of solution of platinum chloride, rapidly and completely reduces nitrobenzene in alcoholic solution to aniline, giving a solution which can be at once decanted and tested with bleaching powder.

By the electrolysis of a solution of nitrobenzene in concentrated sulphuric acid amido-phenol sulphonic acid forms at the cathode.

The following methods of detecting small quantities of nitrobenzene are due to Jacquemin. A single drop of nitrobenzene dissolved in 20 c.c. of alcohol is stated to suffice for all three tests:

a. The liquid is treated with zinc and sulphuric acid to reduce the nitrobenzene to aniline. The liquid is treated with excess of sodium carbonate and filtered; to the filtrate 1 drop of carbolic acid is added, and then some sodium hypochlorite, when a brown colouration, rapidly changing to blue, due to formation of sodium erythrophenate, indicates the presence of nitrobenzene.

b. The liquid is treated with some lead dioxide. If excess of the oxide be used, a rose tint, changing to brown, is developed, but otherwise the rose colour changes to blue. The reaction is said to be very delicate.

c. A crystal of potassium chlorate is added to the liquid, and a drop of concentrated sulphuric acid allowed to run down the side of the tube, when a violet colouration is produced.

Toxicological Detection of Nitrobenzene.—The symptoms produced by nitrobenzene, when taken either in the liquid or the gaseous state, show that it is an active poison of a peculiarly insidious nature. For the most part its action is that of a powerful narcotic, and, as a rule, it produces but little local irritation of the stomach or bowels. The first symptoms are usually headache and drowsiness, followed by flushing of the face, difficult breathing, irregular pulse, dilatation of the pupils, more or less loss of voluntary power, and sometimes convulsions. On attempting to walk the poisoned person will sometimes reel as if drunk, and the breath will smell of nitrobenzene. These symptoms are followed by coma, which may come on slowly, but is more frequently sudden, increasing in intensity until death ensues in 5 or 6 hours from the commencement of the symptoms. When the stage of coma is reached there is but little chance of preventing a fatal termination of the case. On the whole, the symptoms of poisoning by nitrobenzene simulate those of apoplexy, but the strong and persistent odour

and the intense salivation it is apt to produce sufficiently distinguish it from the latter affection.

The vapour may prove injurious even when largely diluted with air.

The *post-mortem* appearance of the stomach is normal, but the smell of the poison will usually be perceptible, unless death has ensued by inhalation of the vapour. The brain is always congested, and the blood everywhere black and thick, but fluid, the heart being full of dark, treacly blood. There is usually well-marked and long-continued rigidity. In cases of delayed death, nitrobenzene may not be found as such on analysis, owing to its reduction to aniline, which will be met with in the brain and urine. In many cases a distinct colour will be observed on the skin, at least in some parts.

The poisonous effects of nitrobenzene are identical with those of aniline, and are most probably due to the reduction of the nitrobenzene to that substance in the body.

For the detection of nitrobenzene, the portions of the body to be examined should be reduced to fragments and acidified with dilute sulphuric acid. The liquid is distilled, and the distillate examined from time to time, with the view of detecting the presence of any unchanged nitrobenzene. Then treat the contents of the retort with rectified alcohol, and filter. Precipitate the filtrate with excess of basic lead acetate, and again filter. Remove any lead from the liquid by adding a slight excess of sodium sulphate. Evaporate the filtered liquid nearly to dryness, and render the solution alkaline with sodium carbonate. Then agitate with ether to dissolve the aniline, run off the aqueous liquid, and agitate the ethereal solution with a little very dilute sulphuric acid. Separate this acid layer, which will contain any aniline as sulphate, concentrate by evaporation at a low temperature, and test for aniline by bleaching powder solution as described on page 212.

Commercial Nitrobenzol.—The products obtained on a large scale by the action of nitric acid on commercial benzols vary in composition with the character of the benzols employed in their manufacture, but are often exceedingly complex, containing simultaneously several isomeric varieties of the different mono- and dinitro-derivatives of the benzene series of hydrocarbons, which diminish in volatility and fusibility with the number of atoms of carbon or molecules of NO_2 contained in them. By the action of reducing agents the various nitro-compounds yield aniline and other bases, the constitution

of which depends on that of the nitro-compounds from which they are derived. Some of these yield colouring matters materially differing in shade or brilliancy from those given by purer products.

The presence of hydrocarbons in nitrobenzol may be detected by dissolving 30 c.c. of the sample in 70 c.c. of concentrated sulphuric acid, in which it ought to be entirely soluble.

Commercial nitrobenzene and dinitrobenzene commonly contain the nitro-derivatives of thiophene. These impurities may be detected by dissolving the sample in alcohol, and adding a single drop of aqueous potassium hydroxide, when a deep-red solution is obtained, a thin layer appearing violet. An excess of alkali destroys the colour, but it may be restored by cautious neutralisation.

The sp. gr. of nitrobenzol made from 90% benzene should be 1.186, and from 30 to 40% benzol 1.175 to 1.190.

TOLUENE.

Methylbenzene, $C_7H_8 = C_6H_5CH_3$.

Toluene, formerly called "toluol,"—a name which should be applied only to the commercial substance,—is obtainable by various synthetical methods, is a product of the dry distillation of tolu-balsam and many other resins, and is present to a considerable extent in coal-tar naphtha. It closely resembles benzene. The chief points of difference are:

1. The *odour*, which is distinct from that of benzene.
2. The *sp. gr.*, 0.881 at 0°, 0.871 at 15°.
3. The *b. p.*, 111°, is considerably higher than that of benzene.
4. The *solidifying point*, toluene remaining liquid even at —20°, while benzene is solid at 0°.

By the action of concentrated nitric acid, toluene is converted into one or more nitrotoluenes, or dinitrotoluenes; but when boiled with dilute nitric acid it is oxidised with formation of benzoic acid and other products. Commercial nitrotoluol has a sp. gr. of 1.167. Pure orthonitrotoluene has a gravity of 1.162, that of metanitrotoluene being 1.168. Paranitrotoluene is solid at ordinary temperatures. Dinitrotoluene is used for deblooming oils.

When treated with excess of hot concentrated sulphuric acid, toluene forms 2 isomeric toluenesulphonic acids, $C_7H_7HSO_3$. On heating the liquid to about 160°, and passing a current of steam, these compounds are decomposed and the toluene distils over almost without loss.

COMMERCIAL TOLUENE.

Toluene constitutes the greater part of "50% benzol" (page 228), and also occurs to a considerable extent in "90% benzol."

Toluene occurs in an approximately pure state in commercial "toluol," which is now manufactured on a large scale. When fractionated in the manner described on page 208, commercial toluols should give the first drop at 110° to 111°, and 90% of distillate below 120°.

An almost pure toluene is now made commercially, which distils wholly within a degree or two of 110°.

XYLENES.

Dimethylbenzenes. $C_8H_{10} = C_6H_5 . (CH_)_2$.

All 3 forms of xylene (see page 229) occur in coal-tar; the isomeric body, ethylbenzene, $C_6H_5(C_2H_5)$, has also been found by some investigators.

The isomeric xylenes present a close general resemblance to benzene and toluene, but are distinguished by their higher b. p., lower sp. gr., and the greater facility with which they are oxidised and are converted into sulphonic acids.

The different behaviour of the isomeric xylenes with reagents has some practical interest as affording a means of examining the nature of—

Commercial xylene or xylol, which is now manufactured on a considerable scale for the preparation of cumidine (by heating the monomethyl-metaxylidine hydrochloride with methyl alcohol) and of azo-colouring matters (scarlets, oranges, etc.). Commercial xylene is obtained by the fractional distillation of coal-tar naphtha. It varies greatly in purity, giving 90 to 95% within a range of 2° to 6° from the first drop over. The distilling-points may range from 136° to 138°; 136° to 140°; 136° to 142°; 138° to 140°; or 138° to 142°, according to the stipulations of the contract note. In some cases the contract note stipulates that 90% of the sample of xylene shall distil within a range of 1°, and this behaviour is very strictly enforced.

Besides varying proportions of the three xylenes, the properties of which have already been described, commercial xylol contains more or less of the lower and higher homologues (methylbenzene, 1-3-4-

and 1-3-5-trimethylbenzenes), together with a notable proportion of paraffins, and probably ethylbenzene and ethenylbenzene and hydrocarbons of other series. The hydrocarbons of the olefine and acetylene series are not improbably present in the fraction of crude naphtha from which commercial xylene is prepared, but they either suffer absorption by the sulphuric acid used for the purification, or are thereby polymerised so as to remain in the retort when the purified substance is redistilled. Orthoxylene also undergoes absorption by the sulphuric acid employed, and hence the refined product contains a comparatively small proportion of this hydrocarbon, the same reaction having prevented its recognition in coal-tar until recently. Thioxene, or dimethylthiophen, C_6H_8S, if present, will also be absorbed by treatment with sulphuric acid. On the other hand, metaxylene hexahydrides and homologues behave in all essential respects like paraffins.

Of all these constituents of commercial xylene, the *metaxylene* is the only one of value, even its 2 isomers being useless. If the meta-xyene contain even a few units % of orthoxylene, on converting it into the nitro-derivative, and this into xylidine, tarry matters are formed which are a serious inconvenience in practice.

The table on page 218 shows some points of difference between the xylenes. The reagents named are prepared as follows:

Chromic Acid Mixture.—A solution of 8 grm. of potassium dichromate in a mixture of 10 grm. of sulphuric acid and 90 c.c. of water.
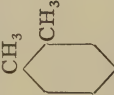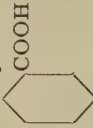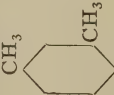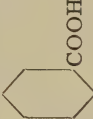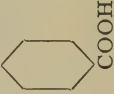
Diluted Nitric Acid.—Nitric acid (sp. gr. 1.4), diluted with twice its volume of water.

Nitric-sulphuric Acid Mixture.—Equal measures of fuming nitric acid (sp. gr. 1.5) and concentrated sulphuric acid are mixed and allowed to cool.

The first 2 reagents are applied by boiling the hydrocarbon with excess under an inverted condenser for several hours. For oxidation of metaxylene a temperature of 150° is desirable.

The nitric-sulphuric acid mixture is used cold, the hydrocarbon being gradually added and the product allowed to stand some hours. It is then poured into an excess of water, the liquid passed through a wet filter, the separated nitro-derivatives recrystallised from boiling alcohol and examined under the microscope.

The following method for the assay of commercial xylene is due to J. M. Crafts (*Compt. rend.*, **114** (1892), 1110.

(For preparation of reagents, see page 217.)
Results of action of

Name	Solidifying point, °	B.p.,°	Diluted sulphuric acid	Chromic acid mixture	Diluted nitric acid	Cold mixture of nitric and sulphuric acids
Orthoxylene 1-2 dimethylbenzene CH₃ CH₃	Below −22	142 to 143	Easily soluble	Entirely decomposed	Orthotoluic acid CH₃ COOH	Liquid products
Metaxylene 1-3 dimethylbenzene CH₃ CH₃	....	137 to 140	Soluble	With difficulty, Isophthalic acid COOH COOH	With difficulty, Isophthalic acid	Trinitrometaxylene, $C_6H(NO_2)_3(CH_3)_2$
Paraxylene 1-4 dimethylbenzene CH₃ CH₃	15	136 to 137	Insoluble	Terephthalic acid COOH COOH	Paratoluic acid CH₃ COOH	Trinitroparaxylene, $C_6H(NO_2)_3(CH_3)_2$

A weighed amount of the sample (10 to 20 grm.) is poured on 2.5 times its weight of concentrated sulphuric acid in a tube of hard glass. The depth of the xylene layer in millimetres is noted, the tube is sealed and heated to 120°, with occasional violent shaking. The tube is allowed to cool, opened, 3 or 4 measures of a mixture of equal parts of hydrochloric acid and water added, the mixture shaken well and allowed to stand for an hour at room temperature. An insoluble layer of saturated hydrocarbons is formed. This is measured and separated in a separatory funnel, the solvent acid returned to the tube, which is resealed and heated to 122° for 20 hours. By this treatment 97% of the 1-3-xylene forms a layer, which can be measured, and after separation distilled and weighed. A small amount of impurity is removed by distillation. The 1-2- and 1-4-xylenesulphonic acids undergo but little decomposition at 122°, but at 175° the hydrocarbons are regenerated. If these be dissolved in 3 parts of concentrated sulphuric acid, the solution cooled, and 1 part of concentrated hydrochloric acid added, 1-4-xylenesulphonic acid is thrown down in crystals, which should be collected on an asbestos filter, washed with concentrated hydrochloric acid until the washings no longer react with barium chloride, and the precipitate allowed to dry in the air to constant weight. The crystals have the composition $(C_8H_9SO_3H)_2 + 3H_2O$; the weight multiplied by 0.4977 gives the xylene. For direct estimation of 1-2-xylene, Levinstein[1] advises the following method: 100 c.c. of the sample are shaken thoroughly with 120 c.c. cold concentrated sulphuric acid until no further solution of hydrocarbons occurs. It is best to cool the mixture. The 1-2- and 1-3-xylenes are converted into sulphonic acids, but the 1-4-xylene is unaffected and separates unchanged. The acid liquid containing the 2 sulphonic acids is then separated, and these converted into their calcium and then into their sodium salts. On concentrating the solution of the latter, sodium 1-2-xylenesulphonate will crystallise in large, flat prisms, while the 1-3-salt remains in solution. The mother liquor should be further concentrated, when a second crop of crystals will be obtained. Both crops are purified by resolution and recrystallisation. The indistinct crystals of the 1-3-form are readily distinguished from the large, well-defined crystals of the 1-2-salt from English crude xylols. That from Scotch products crystallises far less readily, probably owing to an admixture of some foreign sulphonate. Crystallised sodium 1-2-xylenesulphonate contains $C_6H_3(CH_3)_2SO_3Na + 5H_2O$. It is dried by pressure between folds of filter-paper, and then

[1] *J. Soc. Chem., Ind.,* 1884, 77.

over sulphuric acid, when it can be weighed, if desired. The xylene can be regenerated by adding excess of sulphuric acid and distilling in a current of steam at 120° to 150°.

It might be preferable to saturate the acid liquid with barium hydroxide solution, filter from the sulphate, and crystallise the sulphonates from the filtrate. Barium 1-2-xylenesulphonate crystallises in large, nacreous laminæ, requiring 3 parts of boiling water or 18 parts of cold water for solution.

Samples 2 and 5 were analysed independently by the same methods by A. Rademacher, with the following results:

Number	1-2-xylene	1-3-xylene	1-4-xylene	Paraffins
2	14.5	81	3	1.5
5	3	$\begin{cases} 87 \\ 86.5 \end{cases}$	4.5	$\begin{cases} 8 \\ 6 \end{cases}$

The following figures were obtained by Levinstein, but partly by methods different from those above described:

No.	Origin of sample	Sp. gr. at 19°	Distilling degrees;	Percentage of			
				1-2 xy-lene	1-3 xy-lene	1-4 xy-lene	Par-affins
1	From Manchester tar.......	0.8629	134–140	4	87	.6	3
2	From English tar...........	0.8660	138–141	15	79	3	3
3	From Scotch tar...........	0.8574	134–140	12	72	8	8
4	From mixed English and Scotch tars.	0.8605	134–141	3	81	10	6
5	From mixed English and Scotch tars.	......	140–141	5	86	3	6
6	Unknown..................	......	139–141	15	70	5	10
7	Pure metaxylene isolated by dilute nitric acid, etc.	0.8668	142–143	0	100	0	0

COAL-TAR NAPHTHA.

In the first distillation of coal-tar 2 fractions are obtained, known respectively as "first light oils" and "second light oils." Sometimes they are not collected separately, in which case the fraction is known as "crude naphtha" or "light oil." Good "first light oils" or "first runnings" ought, on redistillation, to yield 10% below 100° and an average of 78% below 170°. On again distilling the fraction collected under 130° fully 25% should come over under 100°. "Second light

oils" should have a density of about 0.975. It yields but little distillate below 120° and about 30% below 170°.

Crude coal-tar naphtha is a more or less fluorescent liquid, of a dark coffee colour and disagreeable odour. It has a density of 0.840 to 0.940, or even higher, and evolves ammonia abundantly on distillation. It is an extremely complex product, as will be seen on reference to the table on page 198. Many or all of the bodies boiling below about 220° are sometimes present simultaneously. The sp. gr. of crude naphthas of London make usually ranges between 0.883 and 0.888, and that of Scotch naphthas from 0.868 to 0.876, but the density is sometimes considerably outside these limits.

Crude naphtha is usually submitted to redistillation without previous chemical treatment, the resultant products being "once run naphtha" and "last runnings."[1] By some distillers an intermediate product is obtained, termed "medium naphtha." It is the fraction of the crude naphtha which on redistillation passes over between 160° and 180°. Benzene can be isolated in small quantity even from this fraction by the use of a dephlegmating arrangement.

Once-run naphtha is a fluid of a more or less amber-yellow colour, and a sp. gr. ranging from 0.886 to 0.892. The method of assaying once-run naphtha by distillation is described on page 207 *et seq.*

Before redistilling once-run naphtha on a large scale it is purified by treatment with sulphuric acid of 1.845 sp. gr. This removes the bases, hydrocarbons of the olefine and acetylene series, and some of the higher homologues of benzene. A subsequent treatment with lime or sodium hydroxide eliminates the phenols and any other bodies of acid character. The oil is then washed with water and again distilled.

Once-run naphtha is the starting-point from which the manufacturer derives, by fractional distillation, the following products: 100% benzol; 90% benzol; 50 and 90% benzol (called "50/90 benzol"); 30% benzol; solvent naphtha; burning naphtha; and a further quantity of last runnings. Each of these products has distinctive characters by which it is known and recognised commercially. In addition, benzene, toluene, and xylene are now manufactured on the commercial scale in a condition of high purity.

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[1] "Last runnings" are highly charged with naphthalene, and find an application as a common burning oil in street vapour-lamps. A sample examined by B. Nickels gave, on fractional distillation, 10% at 142°; 20 at 146°; 30 at 151°; 40 at 157°; 50 at 164°; 60 at 170°; 70 at 179°; 80 at 191°; and 90 at 209°. When 70% had passed over, naphthalene appeared in quantity. By repeated fractioning, evidence of the presence of toluene and xylene was obtained.

Burning naphtha is a product similar to "last runnings," but results from a second distillation. It should have a sp. gr. of 0.880 to 0.887, and should give 20 to 30% over at 150°, and 90 at 170°.

Solvent naphtha is so called from its wide application as a solvent for india-rubber in the manufacture of waterproof articles. It is also used for washing crude anthracene. It gives from 8 to 30% of distillate below 130°, and about 90 below 160°. The sp. gr. should not exceed 0.875. Solvent naphtha has a complex and variable composition, but consists chiefly of isomeric xylenes and cumenes, with a notable proportion of paraffins, and sometimes several units% of naphthalene, the last constituent being considered very objectionable. Formerly, solvent naphtha comprised the whole of the fraction from the redistillation of once-run naphtha passing over above the benzols and below 160°, but when a demand arose for xylene as a separate product, much of it was removed, with the result of rendering the residual solvent naphtha less suitable for its intended purpose.

Carburreting naphtha is a product consisting chiefly of xylenes. It is usually specified as giving at least 70% of distillate at 130° and 90 at 150°, the sp. gr. ranging from 0.850 to 0.870.

Commercial Benzols.—In commerce, the term "benzol" is applied generically to the more volatile portions of redistilled coal-tar naphtha. It is a convenient name to indicate this more or less complex liquid, consisting chiefly of benzene and its homologues; while the use of the term "benzene" should be restricted to the definite hydrocarbon of the formula C_6H_6.

Commercial benzols consist essentially of mixtures of very variable proportions of benzene and its homologues, together with: smaller percentages of carbon disulphide; certain light hydrocarbons technically known as "petroleum," and which are incapable of nitration, consisting largely of pentene; thiophene and its homologues; traces of water; acetylene, and probably homologues; and impurities of an indefinite nature.

The light hydrocarbons diminish the yield of colouring matter from the aniline made trom the benzols containing them, and, if present in considerable proportion, render the process of nitration irregular and even dangerous. Carbon disulphide is a somewhat troublesome impurity, and is difficult to get rid of by ordinary means.

The details of the method of effecting the assay of benzols are given on pages 209, 230 *et seq.* According to the behaviour of the sample

when distilled, it is classed as 100% benzol, 90% benzol, 50% benzol, or 30% benzol.

90% **Benzol** is a product of which 90% by volume distils before the thermometer rises above 100°. A good sample should not begin to distil *under* 80°, and should not yield more than 20 to 30% at 85°, or much more than 90% at 100°. It should wholly distil below 120°. An excessive distillate—*e. g.*, 35 to 40% at 85°—indicates a larger proportion of carbon disulphide or light hydrocarbons than is desirable. The actual percentage composition of a 90% benzol of good quality is about 70 of benzene, 24 of toluene (including a little xylene), and 4 to 6 of carbon disulphide and light hydrocarbons. The proportion of real benzene may fall as low as 60 or rise as high as 75%. 90% benzol should be colourless ("water-white"), and free from opalescence.

The sp. gr. of English 90% benzols ranges from 0.880 to 0.888 at 15.5°, but the figure is no indication of the quality of a sample, owing to the presence of carbon disulphide and light hydrocarbons, which, from their high volatility, become concentrated in this class of benzol. Since carbon disulphide has a sp. gr. of 1.27 and the light hydrocarbons ("petroleum") average 0.860, the 2 may in certain proportions exactly compensate and be without effect on the sp. gr. of the product. Watson Smith examined a 90% benzol which had a sp. gr. of 0.900 and contained 6% of carbon disulphide. After removing this impurity the sp. gr. of the benzol fell to 0.880.

Scotch 90% benzols contain but little carbon disulphide, but a considerable proportion (7 to 8%) of light hydrocarbons; hence the sp. gr. is often as low as 0.870 or even less. The first 20% distilled from such a sample may have a density of 0.866; while the residual 80% will be as dense as 0.872. The low density of the first fraction here distinctly indicates "petroleum," and not carbon disulphide, as the predominant impurity. By eliminating the carbon disulphide from 90% benzol in the manner described on page 226, the anomaly in the sp. gr. almost disappears, and the interpretation of the results of the fractional distillation becomes much simpler. The sp. gr. is about 0.880 to 0.882. The sp. gr. of the United States 90% benzols is about 0.879 to 0.882.

C. P. crystallisable and 100% benzol are products made in the United States. The first mentioned is very nearly pure benzene and can be crystallised by chilling to 50°. On distillation by the method described on page 208 it should all pass over within 2° (distilled to

dryness). The reviser of this edition has found that 90% will often distil over within 1/2° if the vapours in the bulb are carefully protected against superheating. The sp. gr. should be 0.882–0.884. The 100% benzol is a product which all distils below 100°. The chief constituent other than benzene is toluene.

50% **benzol,** often called 50/90 benzol, a product of which 50% by volume distils over at a temperature not exceeding 100°, and 40% more (making 90 in all) below 120°. It should wholly distil below 130°. The density of English 50% benzol is about 0.878 to 0.880 of Scotch 0.867 to 0.872 and of the United States 50% 0.870 to 0.876. This class of benzol is nearly free from carbon disulphide, and contains comparatively little of the light hydrocarbons, while the proportion of toluene and xylene is, of course, larger than in 90% benzol. 50/90 benzol is employed for producing the heavy aniline used for preparing rosaniline or magenta.

In the case of a benzol of intermediate character, the proportions of 90% and 50% benzol to which it corresponds may be found by the following rule: Deduct 50 from the percentage-volume of the sample distilling below 100°, and multiply the difference by 2.5. The product gives the percentage of 90% benzol in the sample, the difference between this and 100 being the proportion of 50% benzol. Thus, a benzol giving 64% over below 100° corresponds to a mixture of 35 parts of 90% benzol with 65 parts of 50/90 benzol; for:

$$64 - 50 = 14; \quad 14 \times 2.5 = 35; \text{ and } 100 - 35 = 65.$$

For English benzols the rule is accurate to 1%.

30% **benzol** is a product of which 30% distils below 100°, about 60% more passing over between 100° and 120°. It consists chiefly of toluene and xylene, with smaller proportions of benzene, cumene, etc. The sp. gr. should be about 0.875.

For the manufacture of aniline-red, magenta, or fuchsine, a benzol is required which will yield (by nitration and subsequent reduction) an aniline oil of which 3/4 distils between 180° and 190°, and the remainder between 190° and 215°. Such an aniline oil is producible from a benzol of which 3/4 passes over between 80° and 100°, and the rest between 100° and 130°. For the manufacture of methyl-violet, on the contrary, an aniline as free as possible from higher homologues is required, and this must be made from a benzol which almost wholly distils below 83° or 84°. For xylidine-red an aniline oil derived from

benzols boiling above 115° or 120° is required, but it is often found preferable to prepare this by fractionating an ordinary aniline oil rather than to employ a benzol of specially high b. p. for the purpose. The commercially pure xylene and toluene now extensively manufactured have, to a great extent, replaced the high boiling "benzols" formerly employed.

The "benzol" of the British Pharmacopœia (1898) is defined as a mixture of about 70% of benzene and 20 to 30% of toluene, having a sp. gr. of from 0.880 to 0.888. It should begin to distil at 80°; 90% should pass over below 100° and should wholly distil below 120°.

The benzol of the United States Pharmacopœia is pure benzene or, approximately, the *Benzol* C. P. crystallisables described on page 223. "Benzene, C_6H_6, is a colourless, transparent liquid of a peculiar, aromatic odour, sp. gr. 0.871 at 25°, congealing at 5.2°, and boiling at 80.4°. It is insoluble in water, but soluble in 4 parts of alcohol and in ether. When equal volumes of benzene and concentrated sulphuric acid are mixed, the latter should not become coloured. On shaking 2 c.c. of benzene with 0.5 c.c. of sulphuric acid and 1 drop of fuming nitric acid, no green or blue tint should be produced (absence of thiophene).

Assay of Commercial Benzols and Naphthas.—The observations of importance in judging of the quality of a commercial benzol or naphtha are, in addition to the appearance and smell of the sample: its sp. gr. its behaviour with concentrated sulphuric acid; the proportion of carbon disulphide; the proportion of the light hydrocarbons, technically known as "petroleum"; the proportion of nitratable hydrocarbons; and its behaviour on fractional distillation. In the case of commercial xylols, the proportion of metaxylene should be ascertained in the manner directed on pages 219 and 220.

Commercial 90% benzol should not be diminished in volume by more than 1/2% when agitated with 5% by measure of cold concentrated sulphuric acid. For a more stringent test, applicable to commercially pure benzene, see page 209.

Water, if present in such quantity as to render the sample turbid, must be got rid of prior to any further process of assay. This may be done sufficiently perfectly by passing the liquid through a dry filter. A complete elimination of the water may be easily effected by agitating the sample with a little recently gently ignited plaster of Paris, and filtering. The dehydration is almost instantaneous. If a known

weight of plaster be employed, and it be afterward washed with a little gasolene, dried at a gentle heat, and reweighed, a determination of the amount of the water may be readily effected.

Carbon disulphide often exists in very sensible quantity in crude and once-run naphtha, and in 90% benzol. From the less volatile classes of benzol it is usually absent. Its presence is important only in 100% and 90% benzol. Carbon disulphide may be detected by a method of Votocek and Votmessil (*Chem. Zeit. Rep.*, **25**, p. 275 (1901)). Hofmann's reaction, $CS_2 + 2C_6H_5NH_2 = CS(NHC_6H_5)_2 + H_2S$, is the basis of this test. In the presence of ammonia the reaction is said to proceed rapidly, requiring about 15 minutes for the completion of the test. The ammonium sulphide is detected by the nitroprusside reaction. According to Lunge ("Coal-tar and Ammonia," 3d Ed., p. 614), the best test for carbon disulphide is the phenylhydrazine test, as follows: 10 c.c. of the benzol is agitated with 4 or 5 drops of phenylhydrazine for 1 to 1 1/2 hours. With 0.2% CS_2 a thick precipitate forms, but even with 0.03% the precipitate is easily seen.

The presence of carbon disulphide raises the gravity of benzols considerably, as is shown on page 228. Other simple methods of detecting CS_2 are the formation of crystals of potassium xanthate with alcoholic potash and the formation of ammonium thiocyanate with alcoholic ammonia. This is found by agitating with ferric chloride to give a blood-red colour. Carbon disulphide may be eliminated from benzol, and its amount determined with a near approach to accuracy, by the following method devised by B. Nickels:[1] 100 c.c. measure of the sample of benzol (preferably dehydrated with plaster of Paris, as above described) is treated with a solution of 1 grm. of potassium hydroxide in the smallest possible quantity (about 20 c.c.) of hot absolute alcohol, and the mixture agitated thoroughly. If carbon disulphide be present, a yellow colour is usually developed, and the mixture becomes pasty from the formation and separation of potassium xanthate in crystals of a characteristic silky appearance. The mixture is shaken at intervals during half an hour, and is then passed through a dry filter. The adhering benzol is separated as far as possible from the precipitated xanthate by carefully folding the filter and pressing it against the sides of the funnel by means of a spatula. The filtrate is agitated in a cylindrical separator with its own volume of warm water, which removes the excess of alcohol and a little dis-

[1] *Chem. News*, 43 (1881), 148, 250, and 52 (1885), 170.

solved xanthate. If the purified benzol is to be submitted to distilla-tion, it is preferable to operate on at least 200 c.c. of the sample, and treat it a second time with the alcoholic solution of potassium hydroxide, before treating it with water. The aqueous liquid is run off, and the benzol again agitated with its own measure of cold water, after the re-moval of which it may be dehydrated with plaster, and then further examined by fractional distillation.

The potassium xanthate collected on the filter is washed with a little ether, dried at 100°, and weighed. Preferably, it is dissolved in alcohol, the washings from the treated benzol added, and the united solution obtained rendered slightly acid with acetic acid. On adding a solution of copper sulphate, a brownish precipitate of cupric xanthate is formed, rapidly changing to bright yellow cuprous xanthate, $CuC_2H_5(CO)S_2$, insoluble in water and dilute acids. The cuprous xanthate may be collected on a filter, washed, ignited in the air, and weighed as CuO; or the cupric oxide may be ignited with sulphur in hydrogen, and thus converted into cuprous sulphide. The weight of CuO or Cu_2S obtained, divided by 0.523, gives that of the carbon disulphide in the sample operated upon.

Instead of weighing the cuprous xanthate, H. Macagno (*Chem. News*, **13** (1866), 138) titrates the acidified solution of potassium xanthate with a solution of cupric sulphate containing 12.47 grm. of the crystallised salt per litre. The end of the reaction is indicated by the brown colour produced when a drop of the liquid taken out with a glass rod is added to a drop of potassium ferrocyanide solution on a porcelain plate. 1 c.c. of the above cupric sulphate solution corresponds to 0.0076 grm. of carbon disulphide.[1]

A method of estimating CS_2 that has proven satisfactory in the

[1] Macagno's figures, both gravimetric and volumetric, correspond approximately to the ratio Cu : $2CS_2$. This ratio would be readily explicable if the reaction resulted in the formation of cupric xanthate, $(C_2H_5.O.CS.S)_2Cu$; but as the main product is cuprous xanthate, it follows that reduction of the copper occurs, and this must be accompanied with corresponding oxidation of a portion of the xanthate. According to H. Debus, the yellow precipitate is a compound of cupric xanthate with cuprous sulphide, but this is very improbable. The copper salt of the acid $C_2H_5.O.CO.SH$ is also said to be formed together with other products. It is certain that the reaction is very complex and requires further investigation. Experiments made by A. R. Tankard have shown that the ratio Cu : $2CS_2$ is roughly correct, whether the determination be made by titrating with decinor-mal cupric sulphate or by weighing the cuprous sulphide left on igniting the precipitate with sulphur; provided that the copper solution is added immediately after acidifying the xanthate solution, since the free xanthic acid decomposes very rapidly. If the precipi-tation be conducted in alcoholic solution and the precipitate washed with alcohol, a sub-stance is removed which otherwise remains in the precipitate. On diluting the filtrate with water, this body is thrown down in a state of very fine division. It appears to consist, in part at least, of sulphur. From the presence of this and probably of other impurities in the precipitate, this should not be directly weighed. If precipitated from aqueous liquids, it contains the body above referred to, and if thrown down from alcoholic solution, it is contaminated with potassium sulphate, which might be removed by washing with water The process is useful, but the results are not strictly accurate.—A. H. A.

works of the Barrett Manufacturing Co. and communicated to the reviser prior to publication is as follows: Take 5 to 10 grm. of benzol in a weighing bottle of 50 c.c. capacity, add 2.5 c.c. of a saturated solution of potassium hydroxide in absolute alcohol and warm at 60° for 1 hour, using a return-flow condenser. Then wash out into a beaker with warm water and heat on a water-bath until excess of benzol is expelled. The CS_2 has now been converted into potassium xanthate. Add potassium hydroxide and bromine water in large excess and warm until oxidation is complete and the solution is perfectly clear. Then acidify with HCl, boil off the excess of bromine and estimate the sulphur as $BaSO_4$ in the usual way. This method is claimed to give results that are quite accurate and is simple to carry out.

Commercial 50% benzol sometimes contains 0.1% of pyridine and the toluene made from this 0.25%. This pyridine and any other basic substances may be removed by agitating with 10% sulphuric acid. On making this acid extract alkaline with sodium hydroxide, pyridine, etc., may be extracted by means of ether or distilled with steam.

An easily carried out procedure for the estimation of carbon disulphide in benzene is given by I. Bay (*Compt. rend.*, **146,** 132 (1908)): Phenylhydrazine is added to the benzene, forming a precipitate of phenylhydrazine phenyl thiocarbozate, $CS_2(C_6H_5NH.NH_2)_2$. This method is said to give reliable results if the analysis is completed in the course of a day. The precipitation is complete in 2 or 3 hours. The substance is collected on a tared double filter-paper, washed with pure benzene and dried in a vacuum desiccator.

The change in density which results from the elimination of the carbon disulphide from a benzol is very noticeable. Thus, in the case of a sample which would be conveniently classified as a "light 90%" there will be an entire removal of the previous alliaceous odour; a diminution of density from 0.885 to 0.882 or 0.880, according to the amount of carbon disulphide which has been removed; and a disappearance of the abnormally large proportion of liquid distilling below 85°, the reduction in this respect being from 30% or more down to 12%.

The proportion of carbon disulphide eliminated by treatment with alcoholic potassium hydroxide has been proved by B. Nickels to be indicated with a considerable approach to accuracy by the reduction in the sp. gr. of the sample, thus:

1% by volume of carbon disulphide raises the sp. gr. by 0.0033
2% by volume of carbon disulphide raises the sp. gr. by 0.0065
3% by volume of carbon disulphide raises the sp. gr. by 0.0093

The sp. gr. of benzol is not readily determined by the bottle, owing to its high coefficient of expansion. A delicate hydrometer may be used, but the Westphal balance is specially suitable for such determinations. As the sp. gr. of hydrocarbons of the benzene series decreases with the increase in the number of carbon atoms and the b. p. rises, low volatility corresponds with a low sp. gr., though such samples are technically called "heavy benzols."

Instead of determining the light hydrocarbons, it is sometimes of interest to ascertain the proportion of true benzene and its homologues by converting them into nitro-compounds. To effect this, J. von Hohenhausen proceeds in the following manner: A mixture is made of 150 grm. of nitric acid of 1.40 sp. gr. with 200 grm. of sulphuric acid of 1.845 sp. gr. When quite cold, this is gradually added through a tapped funnel to 100 grm. of the sample of benzol contained in a 500 c.c. flask. The liquids are well mixed by agitating the flask between each addition, and cooled if they become warm. When the whole of the acid has been added and the contents of the flask have become cold, the nitrobenzene is separated from the acid, washed several times by agitation with a dilute solution of sodium hydroxide and subsequently with water, the latter allowed to separate completely, and the nitrobenzol produced weighed. A good quality of benzene should not get hot immediately a small portion of the acid is added to it. 100 parts by weight of an English 90% benzol of fair average quality yield not less than 150 parts of well-washed nitrobenzene, while some Scotch benzenes do not give more than 135 parts. The nitrobenzene produced should be further examined by fractionally distilling it, when the last 2% in the retort should remain liquid after cooling. If 100 c.c. of the nitrobenzol be distilled, and the first 30 c.c. of distillate be treated with 70 c.c. of concentrated sulphuric acid, the nitrobenzene and its homologues will dissolve in the acid, while all the unnitrated hydrocarbons will separate. This layer should be again treated with the mixture of sulphuric and nitric acids, when the presence of previously unchanged benzene will be indicated by a rise of temperature. The acid is tapped off, the residual hydrocarbons again treated with strong sulphuric acid, and their volume observed.

Fractional Distillation of Benzols and Naphthas.—The reviser believes the distillation test as carried out in the United States (page 208) is much preferable to the following tests, which

must be given, however, for the benefit of purchasers who buy on such bases.

A fractional distillation in some specified manner is a method of very general application for the commercial assay of benzols and allied products, and, if carefully conducted, and the results interpreted in connection with the sp. gr. and chemical tests, the process affords very satisfactory indications. These indications, however, are of a purely arbitrary character, and, unless the prescribed conditions of manipulation be rigidly adhered to, great discrepancies result. Thus, the barometric pressure, the rapidity of the distillation, the size and shape of the retort, the position of the thermometer bulb, and even its shape and length, are all more or less important factors in the result obtained. On this account it is usual in contract notes to specify minutely the mode in which the test is to be made, and the slightest departure from the prescribed directions may invalidate the contract.

Ordinary Retort Test.—The following "mode of test" is taken *verbatim* from a form of contract note largely employed in commercial benzol transactions: "A quantity of 100 c.c. to be distilled in a glass retort of a capacity of 200 c.c.; bulb of thermometer to be placed 3/8 in. from bottom of retort; distillation to be made over a naked flame, and at such a speed that the distillate shall not pass over in a stream, but as quickly as it can drop in separate particles. Any deficiency in quantity arising from evaporation or other natural causes during the operation to be added to the product at each point, and proper allowance to be made (if necessary) for the observed reading of the barometer."

The proportion by volume of the sample which passes over below and at a given temperature is called the "strength" of the sample at that temperature. For crude naphtha it is usually sufficient to note the volume distilling below 120°; in the examination of once-run naphtha, an observation of the volume distilling below 160° is also made; in the case of 90% benzols the volumes distilled are noted at 84° or 85°, and again at 100°; while with 50 and 30% benzols the temperatures noted are 100° and 120°.

The very great majority of parcels of benzol and naphtha sold in Great Britain are bought, or are supposed to be bought, on the above test; the results obtained by competent operators understanding the test agree closely, the variations rarely exceeding 1.5%.

The following is the best mode of conducting the ordinary retort

test so as to ensure results which are constant and which can be trusted to be as accurate as the process admits. The instructions given apply to the assay of a 90% benzol: The temperature to be observed must, of course, be modified according to the contract note or to the nature of the product under treatment:

100 c.c. of the sample are measured in an accurately graduated cylinder, and poured thence into a tubulated retort of such a size as to be capable of containing 200 c.c. or 8 fluid ounces, when placed in the ordinary position for distillation. The retort should be previously rinsed with some of the sample to be tested, or a little may be distilled in it, and the residue carefully drained out. A delicate thermometer is fitted in the tubulure of the retort by a cork, so that it may be vertical and the lower end of the bulb be 3/8 in. distance from the bottom of the retort.[1] The neck of the retort is then inserted into the inner tube of a Liebig condenser, and pushed down as far as it will go. The condenser should be from 15 to 18 in. in length, and well supplied with cold water. The neck of the retort should not project too far into the condenser; if necessary, it should be cut short. No cork or other connection is necessary between the retort-neck and condenser-tube. Before use, the tube of the condenser should be rinsed with a little of the sample, and allowed to drain, or some of the benzol may be sprayed through it. The graduated cylinder employed for measuring out the sample is next placed under the further end of the condenser tube in such a manner as to catch all the distillate, while allowing it to drop freely. The retort is then heated by the naked flame of a Bunsen burner.[2] The flame should be small, about the size and shape of a filbert, and when the distillation of the benzol commences, must be so regulated that the condensed liquid shall fall rapidly in distinct drops, not in a trickle or a continuous stream.

When the distillation commences, the flame is regulated, if necessary, and the rise of the thermometer carefully watched. The moment it registers a temperature of 85[1] the flame is extinguished. 4 or 5 minutes are allowed for the liquid in the condenser to drain into the measuring cylinder, and then the volume of the distillate is carefully

[1] The thermometer should be 14 in. long; the bulb sufficiently small to ensure its remaining well immersed in the boiling liquid; the first marking or division at 70°, which point should be well out of the tubulure of the retort; and the graduation should be continued up to 130° in benzol-testing. Instruments guaranteed to 0.1 degree, and constructed in the manner above detailed, are now obtainable.
[2] The burner should be furnished with an air-regulator working automatically with each movement of the tap, and should be surrounded with a cylinder to exclude currents of air. The lamp should be placed in a deep tin basin containing sand or saw-dust, in order to absorb the benzol in the event of the retort cracking.

read off and recorded. The lamp is then relighted and the distillation continued till the thermometer rises to 100°,[1] when the gas is turned off as before, and the volume of the distillate read off, after allowing time for drainage. The residual liquid in the retort is allowed to cool, and is then poured, to the last drop, into the measuring cylinder. A deficiency from the 100 c.c. originally taken will generally be observed. This is the loss arising "from evaporation or other natural causes," referred to in the contract note.

The difference between the collective volume after distillation and that of the original sample is to be added to the measure of the distillate collected at each temperature, and the corrected volumes reported as the "strength" of the benzol examined.

Thus, if by distilling 100 c.c. of a benzol there were obtained 20 c.c. at 85° and 90 c.c. at 100°, and the total liquid mixed after distillation measured 99 c.c., the difference between that and 100 c.c.—$i.e.$, 1 c.c.—must be added to the yields at 85° and 100°, respectively, making the corrected figures 21% at 85° and 91 at 100°. As a matter of fact, the loss of volume by distillation is due far more to expulsion of acetylene and other gases than to actual loss of benzol.

In benzol-testing it is very desirable to observe the barometric pressure before making an experiment and to modify the manipulation accordingly. A difference of 1 in. in the height of the barometer makes a difference of about 1° in the b. p. of a benzol. Hence, if the barometer registers 29.5 in. instead of 30 in., the gas should be extinguished so that the thermometer may show a mean temperature of 99.5° instead of 100°.

The foregoing method of testing benzols is admittedly crude and unscientific, but its indications are well understood; and for a time it sufficed for the technical examinations required. Now, however, that a demand has arisen for practically pure benzene, toluene, and xylene, the value of the crude products depends on their content of these hydrocarbons, and hence there is need to replace the test by others giving absolute results.

Modified Retort Test.—A preferable plan to observing the volume

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[1] It is found in practice that, if the light be turned out exactly when the thermometer registers the required temperature, the mercury subsequently rises to an extent varying from 1/2 to fully 1 degree. With a little experience with a thermometer the range of this "after-rise" will become known, and in subsequent operations the lamp should be turned out when the mercury is as much below the required temperature as it is expected afterward to rise above it. Thus, if the after-rise of a thermometer has been found to be 1°, the gas should be turned out when the instrument registers 84.5° instead of 85°, as it will subsequently rise to 85.5°, and hence 85° may be considered to be the mean reading.

of distillate obtained at 1 or 2 temperatures only is to note the height of the thermometer at every 5 or 10 c.c. of liquid which passes over.

Bulb-tube Test.—When there is no contract note to describe the mode of conducting the distillation, it is very much better to substitute for the simple retort a flask fitted with some form of dephlegmator. A very useful arrangement of this kind is that of Le Bel and Henninger (see Vol. 1, page 20), which consists of a number of bulbs, varying from 2 to 6, blown upon a tube, which is fitted by means of a cork to an 8-oz. flask containing the liquid to be distilled. The upper end of the tube is furnished with a tubulure, which can be fitted by a cork to a Liebig condenser, and with an orifice into which a thermometer can be fitted so as to observe the temperature of the vapour which passes over. Each of the bulbs is connected with the one below by a small side-tube. In the constriction of each bulb is placed a little cup of platinum- or copper-gauze, of the size and shape of a small thimble. These cups are made by folding the gauze over the end of a stout glass rod. The ascending vapour condenses in the cups, and thus serves to wash the vapour subsequently as it bubbles through. When the liquid rises to a certain height in each bulb, it runs off by the side-tube, and ultimately finds its way back to the distilling flask, the flame under which is so regulated as to keep all the cups full and cause the distillate to fall in separate drops.

In the improved from of dephlegmator, devised by Glynsky, the wire-gauze is replaced by hollow balls of glass, introduced into the bulbs during manufacture.

Hempel substitutes for the more complex apparatus of Henninger and Glynsky a long glass tube arranged vertically and filled with solid glass beads. This simple arrangement is remarkably efficient.

By employing a dephlegmating apparatus, greatly improved results are obtainable, and a complex liquid may be fractionated at one operation into approximately pure constituents. Hence it is probable that the present empirical method of testing will ultimately be entirely superseded by the more rational process.[1] Almost absolutely pure benzene, toluene, and xylene are now articles of commerce, being produced on a large scale by a single apparatus based on the principle of the bulbed tube, known as column stills; and it will be necessary to

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[1] The use of a dephlegmator in fractionating benzols is universal in German laboratories, tubes having as many as 12 bulbs on the same stem being sometimes employed. 1000 c.c. is the quantity usually employed for this test, and the distillation is conducted in a copper vessel.

ascertain the percentage composition of the benzols used in their production. This is approximately possible by operating with the bulb-apparatus, especially if the carbon disulphide be previously removed, but it is wholly beyond the powers of the ordinary retort.[1]

	A Commercial 90% benzol in 8-oz. retort.	B A., in 8-oz. retort, after being purified from CS_2	C B., Distilled in flask with 3-bulb apparatus
Sp. gr. at 15.5°......................	0.884	0.881	0.881
First drop distilled at.................	79.5°	83.4°	....
5% over at............................	....	84.2	81.25°
10% over at............................	....	84.3	82.0
20% over at............................	....	85.0	82.8
25% over at............................	84.0	....	....
30% over at............................	85.0	85.8	83.0
40% over at............................	85.4	86.4	83.5
50% over at............................	86.4	87.1	84.7
60% over at............................	88.0	88.3	85.3
70% over at............................	90.0	90.0	86.5
80% over at............................	93.0	93.0	89.3
90% over at............................	100.0	100.0	100.0
95% over at............................	....	112.4	111.8

When the original sample A was fractionated in the 3-bulb apparatus at 45°, it gave oily drops indicative of carbon disulphide; and these became more abundant at 60°. At 70°, 5 1/2% had distilled, and the thermometer rose at once to 80°. The process being stopped at this point, the contents of the flask were found to have decreased in density from 0.884 to 0.882, showing the removal of a substance heavier than benzene. That this was largely carbon disulphide is proved by the figures in column B, the complete removal of the impurity reducing the gravity and raising the b. p. When the purified sample B was fractionated by the 3-bulb apparatus into 20, 70, and 10% portions, they showed a density of 0.883, 0.885, and 0.8715, respectively. Had carbon disulphide been present, the first fraction would have been denser instead of lighter than benzene (sp. gr. 0.885). Hence the first portion of the distillate must have contained light hydrocarbons ("petroleum"). By operating originally on 300 c.c. of the same sample, removing the carbon disulphide by alcoholic potash, and several times repeating the process of fractionating with the 3-bulb apparatus, Nickels obtained the following results as indicative of the proximate analysis of the benzol tested:

Carbon disulphide, removed by alcoholic potash........................ 1.5%
Light hydrocarbons, sp. gr. 0.860 (more or less non-nitrofiable; probably
    chiefly pentene and acetonitrile) 3.5%
Benzene, sp gr. 0.885, and distilling wholly within a range of 2°.........78.4%
Toluene, sp. gr. 0.8715, and distilling within 2°....................... 16.6%
                                                                        100.0%

If 400 or 500 c.c. of the sample of benzol be carefully purified from carbon disulphide by treatment with alcoholic potassium hydroxide and then fractionated with the aid of a 6-bulb tube, the light hydrocarbons can be concentrated in a comparatively small volume distilling between 60° and 70° C. The lightest of these impurities have a sp. gr. of 0.760, and such a product is readily obtainable by again fractionating that first obtained. Nickels has pointed out that if 0.760 be taken as

[1] The annexed figures are communicated by Mr. B. Nickels. Column A represents the temperatures recorded by the thermometer when the *original* benzol was distilled in an 8-oz. retort in the ordinary way; B shows the alteration produced *by removing the carbon disulphide* in the manner described on page ; 226 and C shows the results obtained when the *purified* benzol was distilled in a 3-bulbed apparatus instead of in a retort.

the mean sp. gr. of the light *hydrocarbons*, the proportion of these present in commercial 90% benzol may be deduced with a considerable approach to accuracy from the sp. gr. of the sample previously purified from carbon disulphide. Thus a mixture of 70 measures of pure benzene with 30 of pure toluene (which is the proportion in which they usually exist in 90% benzol) has a sp. gr. of 0.8805, which would therefore be that of the sample purified from carbon disulphide if no light hydrocarbons were present. Each 1% of impurity of 0.760 sp. gr. reduces the sp. gr. of the mixture of about 0.0012. Thus the synthetic sample described on page 238, containing 8% of light hydrocarbons, had, after removal of the carbon disulphide, a sp. gr. of 0.8710. (0.0012×8=0.0096; and 0.8805−0.0096=0.8709; or 0.8710 nearly.) *Thiophen* is not commonly present in benzol in sufficient proportion to affect the figures obtained as above; but if existing in quantity, as in some carbonisation benzols, it can be separated by agitating the purified sample with 1/10 of its volume of strong sulphuric acid before proceeding to fractionate.

The assay of *crude naphtha* by distillation is not infrequently limited to a determination of the volume percentage obtained at a temperature not exceeding 120°, the operation being conducted in an ordinary retort (page 230). The proportion of distillate usually ranges from 15 to 35%, according to the quality of the naphtha under examination. J. von Hohenhausen gives the following data as representing the distilling points of certain typical crude coal-tar naphthas:

Temperature, °	Percentage of distillate		
	Wigan	Yorkshire	Scotland
105	. . . .	4	. . . .
110	4	16	17
120	19	34	38
130	33	47	49
140	45	. . . .	58
150	55	. . . .	69

Once-run naphtha may be similarly assayed. It usually yields from 40 to 60% of distillate below 120° when examined by the retort method,[1] and an additional 32 to 36% between 120° and 160°

[1] A sample of genuine once-run naphtha yielding 50% over at 120°, when distilled in a retort at a rate of 120 drops per minute, should also yield 50% over below 100° when distilled with a bulb-tube at a rate of 100 drops per minute.

These products, when mixed and redistilled, should yield from 19 to 26% over at 100°. For technical purposes the results thus obtained are often sufficient, and their interpretation is well understood. London makes generally give a good yield of 90% benzol, while Midland products are preferable for 50/90 benzols. The results obtained by fractionally distilling a sample of very good once-run naphtha are given below.

A careful inspection of these results shows that crude London naphthas give a low yield by the retort method at 120°, as compared with the yield by the bulb-tube at 100°; while country naphthas give a yield at 120°, by the retort, not much less than, and often considerably exceeding, the yield by the bulb-tube at 100°.

Crude naphthas of London make (*e. g.*, giving by retort method 17% at 100° and 35 at 120°) generally give a good yield of 90% benzol; on the other hand, Midland makes (*e. g.*, giving by retort 10% at 100° and 48 at 120°) are better for 50/90 benzols.

The following figures, communicated by B. Nickels, show the comparative behaviour of typical samples of crude and once-run naphthas when distilled in an ordinary retort and in a flask furnished with a bulb tube. The test may be made on 100 c.c.:

Character of naphtha	By retort method			By bulb-tube method		
	Below 100°	From 100° to 120°	From 120° to 170°	Below 100°	From 100° to 120°	From 120° to 160°
Crude						
London..............	......	12	....	28	....	....
London..............	......	36	....	41	....	....
London..............	......	8,	....	20	....	....
Plymouth	......	46	....	45	....	....
Lancashire..........	......	20	....	25	....	....
Cleckheaton.........	3	44	....	30	23	24
Derbyshire..........	4	43	35	36	20	26
Scotch..............	......	28	....	32	17	37
Once-run						
London..............	......	45	....	43	....	....
London..............	......	66	....	52	....	....
Country.............	......	60	....	45	....	....
Country.............	......	59	....	41	....	....
Country.............	......	58	....	42	....	....
Country.............	......	64	....	46	....	....

G. E. Davis (*J. Soc. Chem. Ind.*, 1885, 647) recommends the following method for the valuation of crude coal-tar naphthas: 200 c.c. of the sample are well agitated for 5 minutes with 20 c.c. of strong sulphuric

acid in a stoppered funnel of 300 c.c. capacity. The mixture is allowed to stand until the acid separates; this is run carefully so that no naphtha is lost. In some cases it is preferable to use 2 washings with successive portions of 10 c.c. of acid each. In either case the naphtha, after drawing off the acid as far as possible, is washed with 2 portions of water (30 c.c. each), then 30 c.c. of 5% sodium hydroxide solution added, and the naphtha again washed with water. The volume of residual naphtha is measured, and after separating it from the washing liquid it is ready for distillation. Davis recommends a 200 c.c. flask with a thermometer and a Le Bel-Henninger or Glinsky fractionating tube, connected with a Liebig condenser delivering into a graduated jar. It is obvious that other standard fractionating apparatus may be employed. The distillation should proceed so that a drop falls every 2 seconds, and be continued until the thermometer reaches 120°, when the receiver is changed and the distillate up to 170° collected. The first distillate consists almost wholly of benzene and toluene, the second portion is "solvent naphtha," the residuum "creosote oil."

In the United States crude naphthas are distilled with dephlegmators, using 200 c.c. or 250 c.c. and making cuts at 100°, 135°–170°.

The simultaneous presence of variable and unknown proportions of carbon disulphide and light hydrocarbons in benzol often completely masks the results of the fractional distillation, and hence B. Nickels strongly recommends that the fractionation should be conducted on a portion of the sample from which the carbon disulphide has been previously removed by treatment with alcoholic potassium hydroxide in the manner described on page 226. The proportion of carbon disulphide present can be estimated by the xanthate formed, or may be deduced from the alteration in the sp. gr. of the sample. B. Nickels prepared a mixture of the following composition, and subjected portions to fractional distillation with and without previous removal of carbon disulphide:

Pure benzene	sp. gr. 0.885,	63% by measure.
Pure toluene	sp. gr. 0.871,	27% by measure.
Light hydrocarbons	sp. gr. 0.760,	8% by measure.
Carbon disulphide	sp. gr. 1.27,	2% by measure.
		100

Columns A and B show the results thus obtained. Column C shows the behaviour of a mixture of 70 volumes of pure benzene with 30 of pure toluene, or, in other words, the mixture without either carbon disulphide or light hydrocarbons:

	A	B	C
	Original mixture	With CS$_2$ removed	Benzene and toluene
Sp. gr.	0.879	0.871	0.8805
First drop collected at	79.0°	82.5°	85.4°
5% collected at		84.0	86.2
10% collected at		85.0	86.6
20% collected at	84.0	86.2	87.2
30% collected at	85.5	87.2	87.8
40% collected at	87.2	88.2	88.8
50% collected at	88.5	89.6	89.8
60% collected at	90.4	91.2	91.4
70% collected at	92.6	93.3	93.2
80% collected at	95.6	96.7	96.2
88% collected at		100.0	
90% collected at	100.0		102.0

These results are very instructive when compared with the figures obtained by B. Nickels from the fractionation of representative commercial samples of different classes of benzols and naphthas. It is interesting to observe the characters of the Scotch 90% benzol, which exhibits an abnormally low sp. gr. owing to the presence of a notable proportion of light hydrocarbons.

From the results yielded by the distillation of the synthetical sample after removal of carbon disulphide (column B.) there is no indication of the presence of 8% of light hydrocarbons, though the low sp. gr. of the sample would point to their presence. This character is dis-

	Good 90% benzol	Good 90% benzol	Scotch 90% benzol	50% benzol	30% benzol	Solvent naptha	Very good once-run naphtha
Sp. gr.	0.8855	0.882	0.873	0.880	0.875	0.877	....
First drop collected at	82.5°	82°	......	.....	.....	......	....
10% collected at	84	83.25	84.5°	94°	97°	128.5°	96°
20% collected at	84.75	84.5	85	95	98	130	99.5
30% collected at	85.5	85	85.75	96.5	99.5	132.5	102
40% collected at	86.25	85.75	86.5	98	101	135	107
50% collected at	87.25	86.75	87.75	100	104	137	111
60% collected at	88.5	88	89	102.5	106	140	119
70% collected at	90.25	89.75	91.25	106	109.5	143.5	128
80% collected at	93.25	92.5	94.75	110.5	113.5	148.5	145
90% collected at	.....	.....	......	120	120	156	170
92% collected at	100	100	100	.....	.....	......	....

guised in the unpurified sample by the presence of the carbon disulphide. As stated on page 238 a good 90% benzol should not begin to distil below 80°, and should not yield more than 20 to 30% of distillate below 85°. The distilling-point is now seldom below 85°, and many 90% benzols are now rectified so as to give the first drop over at 83° to 84°, and the disposition is to go still further, i. e., to 85°. This has not been done voluntarily by the manufacturer, but to meet the demands of continental buyers.

J. von Hohenhausen gives the following data as typical of the behaviour of good average commercial benzols on distillation in an 8-oz. retort:

	90% benzol	50% benzol	30% benzol
Sp. gr.	0.882	0.878	0.875
Distillate at 85°	22%	....	....
Distillate at 90°	74%	....	....
Distillate at 95°	87%	18%	....
Distillate at 98°	....	40%	21%
Distillate at 100°	90%	50%	30%
Distillate at 105°	94%	68%	55%
Distillate at 110°	98%	79%	73%
Distillate at 115°	....	85%	84%
Distillate at 120°	....	90%	90%

G. Lunge (*Treatise on Coal-tar, etc.*, page 290) gives the following figures as his own experience of the behaviour of commercial benzol and coal-tar naphthas when distilled from a fractionating flask with side-tube, the thermometer-bulb being just immersed in the liquid at the commencement of the distillation:

Degrees	90% benzol	50% benzol	Toluol	Carbureting naphtha	Solvent naphtha	Burning naphtha
B. p.	82	88	100	108	110	138
At 88	30	....	....	....	....	....
At 93	65	13	....	....	....	....
At 100	90	54	....	....	....	....
At 110	....	74	56	1	....	....
At 120	....	90	90	35	17	....
At 130	....	....	....	71	57	....
At 138	....	....	....	84	71	....
At 149	....	....	....	97	90	30
At 160	....	....	....	....	....	71.5
At 171	....	....	....	....	....	85

A good knowledge of the composition of crude naphtha may be obtained by distilling 500 c.c. in a retort and collecting the distillate in 2 portions. The fraction passing over below 160° represents the yield of *once-run naphtha*, and that distilling between 160° and 180° the yield of *medium naphtha*. These distillates may then be further fractionated by means of a bulb tube. The fraction of once-run naphtha which on redistillation with a bulb tube passes over below 100° represents 90% *benzol;* from 100° to 120°, *toluol*, commencing to distil at 180° to 110°, and giving 88 to 90% over at 120°; and from 120° to 160°, *solvent naphtha.* The use of the bulb tube for fractionating naphthas has now become general. The indications obtained when once-run naphthas are assayed in the laboratory by this method agree fairly well with the actual yields given on a practical scale, at any rate for 90% benzol and toluol, the determination of solvent naphtha being but rough. The following are results actually obtained:

Laboratory.

Distillate below 100°	= 30%
Distillate between 100° and 120°	= 15%
Distillate between 120° and 160°	= 20%

Works.

90% benzol	= 31 to 32%
90% toluol	= 14 to 16%
Solvent naphtha	= 12 to 15%

The foregoing test may be satisfactorily made on 100 c.c. of the once-run naphtha, but it is preferable to operate on such a quantity as will yield at least 100 c.c. of distillate below 100°, so that this fraction can be proved by a subsequent test to have the actual characters of a 90% benzol. A rule is given below by which the proportion of 90% benzol in a higher boiling product can be deduced.

If a fractionating bulb tube be not at hand, an assay of crude naphtha for the yield of 90% benzol can still be made tolerably satisfactorily by the following process: Distil 500 c.c. of the sample in a glass retort, and collect separately the portion passing over below 180°. This fraction, representing *once-run naphtha*, is then redistilled up to 120°, and the distillate again distilled up to 105°, when the fraction which passes over below this temperature should have the characters of "90% benzol." This, however, should be proved to be the case, when the measure obtained indicates the yield from 500 c.c. of the crude naphtha. If once-run naphtha is to be examined, the first distillation up to 180° should be omitted.

For the *detection of benzene in petroleum spirit* and *vice versa* Holde[1] utilizes the difference of solvent action of the 2 liquids upon a specially prepared asphalt. This is obtained by extracting a Syrian asphalt with petroleum spirit of the highest obtainable gravity until only a faint yellow is imparted to the solvent. This operation can be conveniently carried on in the usual continuous-extraction apparatus. A little of the extracted material is placed in a filter, and some of the liquid to be tested poured on it. The presence of not less than 5% of benzene in a light petroleum of sp. gr. from 0.64 to 0.70, or of not less than 10% in a light petroleum boiling below 35° is shown by a colour imparted to the fluid. Conversely, any considerable amount of petroleum spirit may be detected in benzene by sulphinating (see page 388) or by distilling.

For the quantitative separation of benzenes from petroleum spirit Henriques[2] employs the following process: 5 c.c. of the sample are introduced into a 25 c.c. glass-stoppered cylinder graduated to 0.2 c.c., mixed with 10 c.c. of sulphuric acid, to which 1 grm. (5%) of sulphuric anhydride has been added and shaken until no more of the sample is dissolved. The benzenes are sulphonated and dissolved by the acid, while the petroleum products are but little affected and float on the acid mixture.

Fuming acid is sometimes called "Oleum," containing H_2SO_4 and SO_3, which, calculated to H_2SO_4 amounts to about 105%.

[1] Abst. *Analyst*, 1896, 69.
[2] *Chem. Zeit.*, 1895, 958.

NAPHTHALENE AND ITS DERIVATIVES

By W. A. DAVIS, B. Sc., A. C. G. I.

NAPHTHALENE, $C_{10}H_8$

Naphthalene is formed when a large number of organic compounds (*e. g.*, methane, ethylene, acetylene, acetic acid) are subjected to a red heat in the absence of oxygen. It therefore occurs in coal-tar, which is the sole source from which it is obtained on the large scale.[1] It forms 5 to 10% by weight of the crude tar; a good "middle oil" (b. p. 180° to 230°) should contain at least 30% of naphthalene. Crude naphthalene crystallises from the middle oil on standing and is purified by distillation with steam and subsequent sublimation. On the small scale, for laboratory purposes, the sublimed or steamed naphthalene can be further purified by crystallisation from hot alcohol.

Naphthalene is employed principally in the manufacture of its substitution derivatives (sulphonic acids, naphthols, naphthylamines) which are used in the dyeing industry, and in making phthalic acid (for synthetic indigo, eosin dyes), this being formed by the oxidation of naphthalene by hot fuming sulphuric acid in presence of traces of mercury sulphate. Naphthalene is also used for enriching coal-gas (albocarbon) and as an antiseptic and preservative for woollen goods.

Physical Properties.—Naphthalene crystallises in colourless orthorhombic plates, m. p. 79°, b. p. 218°, sp. gr. (solid) 1.145 at 4°, (liquid) 0.978 at 79.2°. It is practically insoluble in cold and very slightly soluble in hot water; very soluble in boiling alcohol, much less so in cold alcohol (1 in 19 parts of alcohol at 15°). It dissolves very readily in cold chloroform, carbon disulphide, benzene, light petroleum, and phenol. Melted naphthalene dissolves sulphur, phosphorus, and indigo.

Chemical Properties.—With picric acid naphthalene combines to form a crystalline additive compound, $C_{10}H_8$, $C_6H_2(NO_2)_3OH$, m. p.

[1] In the United States it is obtained from carburetted water-gas tar Amer. Ed.

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149°; this fact is utilised in estimating naphthalene (*vide infra*). Concentrated nitric acid converts naphthalene (best when dissolved in glacial acetic acid) mainly into 1-nitronaphthalene; when an excess of acid is used at higher temperatures, various di-, tri-, and tetranitronaphthalenes are formed, according to the conditions. Concentrated sulphuric acid converts naphthalene into either the 1- or 2-sulphonic acid. The former is produced at a low temperature (80°), the latter at a high temperature (160°), best in presence of an excess of sulphuric acid. Prolonged heating with fuming sulphuric acid gives a mixture of the 2:6- and 2:7-disulphonic acids. When naphthalene is heated during a long period with fuming sulphuric acid in presence of a catalyst (mercury) phthalic acid is formed: this action is utilised on the large scale. Chromic acid in acetic acid solution converts naphthalene into 1:2-naphthaquinone. Chlorine and bromine form various substituted chloro- and bromonaphthalenes. Nascent hydrogen reduces naphthalene to dihydronaphthalene, $C_{10}H_{10}$, (sodium in ethyl alcohol), or tetrahydronaphthalene, $C_{10}H_{12}$ (sodium in amyl alcohol). Corresponding with these reduced naphthalenes are naphthalene dichloride, $C_{10}H_8Cl_2$ (prepared from naphthalene by means of potassium chlorate and hydrochloric acid), and naphthalene tetrachloride (formed on passing chlorine into a chloroform solution of naphthalene). The following formulæ show the relationship between these compounds.

$$C_6H_4 \begin{cases} CH:CH \\ | \\ CH:CH \end{cases} \qquad C_6H_4 \begin{cases} CH_2.CH \\ || \\ CH_2.CH \end{cases} \qquad C_6H_4 \begin{cases} CH_2.CH_2 \\ | \\ CH_2.CH_2 \end{cases}$$

Naphthalene   Dihydronaphthalene   Tetrahydronaphthalene

$$C_6H_4 \begin{cases} CHCl.CHCl \\ | \\ CHCl.CHCl \end{cases}$$

Naphthalene tetrachloride
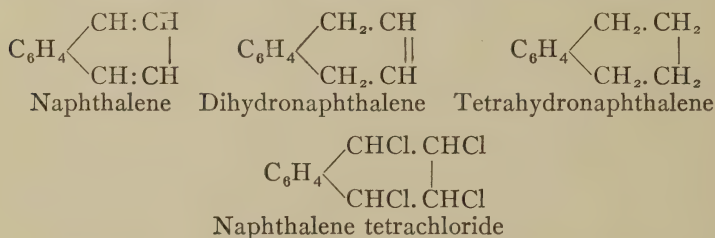
For a systematic review and bibliography of naphthalene derivatives see Reverdin and Fulda's *Tabellarische Uebersicht der Naphthalinderivate* and the Reports of the *Committee on Isomeric Naphthalene Derivatives* of the British Association.

Detection of Naphthalene.—To detect naphthalene in a material thought to contain it (the characteristic smell of naphthalene is a useful index of its presence) the substance is subjected to distillation in a current of steam and the distillate made alkaline with sodium hydroxide to remove phenols; if naphthalene is present it remains undissolved in a

state of greater or less purity. It is characterised by resteaming (if necessary) or crystallising from alcohol, the m. p., characteristic smell, and property of forming a well-defined picrate serving to identify the final product.

Estimation of Naphthalene:

A. *In coal-gas.*

Small quantities of naphthalene are usually present in coal-gas. In cold weather this may crystallise out and cause obstruction in the pipes. The proportion of naphthalene present in the gas is generally estimated by Colman and Smith's method (*J. Soc. Chem. Ind.*, 1900, **19,** 128). This depends on the formation of an additive com-compound of naphthalene with picric acid which is insoluble in dilute aqueous picric acid. The solution of picric acid used is one which is nearly saturated with picric acid at the ordinary temperature (roughly $N/20$): it is standardised by titration with $N/10$ barium hydroxide or sodium hydroxide, using lacmoid as indicator. The absorption of the naphthalene is carried out in three absorption flasks, the first of which has a capacity of 300 c.c. and contains 100 c.c. of the picric acid solution. The second and third are smaller, each containing 50 c.c. of solution. A fourth empty flask should be used to catch any splashings from the third. The gas is bubbled through the series of flasks at the rate of 0.5 to 1 cubic foot per hour until 10 to 15 feet have been passed: it is measured by means of a meter, through which it passes after leaving the absorption flasks. As a portion of the naph-thalene is precipitated as such and not as picrate in the absorption vessels, it is necessary, after the various portions of liquid and precipi-tate have been mixed, to heat the mixture in a closed flask (after evacuating the latter by a water-jet pump) to the b. p. so as to dissolve the precipitate completely, and at the same time prevent loss of naphthalene. The liquid is then allowed to cool, best overnight, and the purified picrate is collected by the aid of a filter pump and washed with a *small* quantity of water. The combined filtrate and washings are made up to 500 c.c., and 100 c.c. titrated with the $N/10$ barium or sodium hydroxide.

229 parts of picric acid combine with 128 parts of naphthalene to form the picrate. The quantity of naphthalene present in the measured volume of gas is thus found by multiplying the weight of picric acid removed from solution by 0.559.

Instead of performing the experiment volumetrically as described above, the precipitate of naphthalene picrate may be dried in a vacuum or in a warm room and weighed (Dickenson Gair). In all cases it is necessary to guard against the condensation of naphthalene in the pipe conveying the coal-gas to the apparatus: this should be as near to the main as possible and be kept surrounded by a steam jacket. With ordinary coal-gas it is also necessary to remove ammonia and bases from the gas before it passes into the picric acid solution. This is effected by means of an oxalic acid solution kept at 80°. When the gas pressure is not sufficient to force the gas through the series of bottles used in the test, it must be increased by artificial means. An ingenious device is described by Colman and Smith (loc. cit.).

Dickenson Gair (J. Soc. Chem. Ind., 1905, 24, 1279, and 1907, 26, 1263) has worked out an alternative method to that given above. In order to avoid heating and re-precipitating the solution of naphthalene picrate, the naphthalene is absorbed from the coal-gas by passing it through acetic acid of sp. gr. 1.644. Picric acid is then added in excess; this causes an immediate separation of pure naphthalene picrate which can be collected and weighed. The modified process can also be carried out volumetrically, this form of procedure being preferable when rapidity is an important consideration. Another modification of Colman and Smith's method consists in collecting on a filter-paper the mixed precipitate of naphthalene and its picrate which is first formed, and washing it into a flask with the smallest possible quantity of strong picric acid solution. Absolute alcohol is then added (50 to 100 c.c.) to dissolve the precipitate and subsequently 300 c.c. of picric acid solution are stirred in so as to precipitate pure naphthalene picrate, which is then dealt with either gravimetrically or volumetrically as above.

B. *In spent oxide of iron* (Gair, loc. cit.). 10 grm. of the undried oxide, roughly powdered, are extracted in a small flask with 100 c.c. of 80% alcohol by shaking well and leaving to stand for 3 to 4 hours. The liquid is filtered into a larger flask and the paper washed once or twice with dilute alcohol. 300 c.c. of strong picric acid solution are added, the flask well agitated and mixture allowed to stand a short time. The naphthalene picrate which separates can be weighed or dealt with volumetrically as above.

C. *Estimation and Testing of Naphthalene in Middle Oil and Carbolic Oil.*

The middle oil is first melted, if necessary, and thoroughly mixed. A weighed quantity (500 to 2,000 grm.) is then left during 24 hours to crystallise, being well stirred at frequent intervals. The crystals which separate are collected by the aid of a vacuum filter, pressed completely free from oil in a small press, and weighed. The b. p. of the naphthalene should be determined by distilling 100 grm. of the pressed crystals and collecting and weighing the various fractions passing over at different temperatures. A good middle oil should contain not less than 30% of naphthalene boiling between 210° and 220°.

The naphthalene in carbolic oil can be estimated by removing the phenols by extracting with aqueous sodium hydroxide, washing the residue with water and allowing the naphthalene to separate from the residual oil as in the case of middle oil.

D. *In phenol.*

The presence of naphthalene in phenol is shown by dissolving away the phenol with dilute aqueous sodium hydroxide: the naphthalene remains undissolved. To estimate the naphthalene in this case the residue obtained is extracted with ether, the ether being then evaporated and the naphthalene weighed, either as such or in the form of its picrate (see above).

Commercial Naphthalene.

Naphthalene is contained largely in the less volatile portions of coal-tar naphtha, in the crude carbolic acid and "creosote oils" which subsequently distil, and in the semi-fluid "anthracene oils" obtained at a still higher temperature. By cooling the portion of the coal-tar distillate which passes over about 200°, naphthalene is frequently deposited in such quantities as to render the product semi-solid. It may be separated by pressure from the liquid oils, and purified by heating strongly with 5 to 10% of concentrated sulphuric acid, washing thoroughly with water, and subliming the product.

Naphthalene is now prepared commercially of high purity, as colourless crystals which distil wholly within a very few degrees of the b. p. of pure naphthalene, and give no pink colour with sulphuric acid. Besides this nearly pure product, which, when remelted and cast into moulds, is employed as "albocarbon," and (under the name "coal-tar camphor") for protecting furs and woollens from moths, naphthalene occurs in commerce as an impure, coarsely crystalline

substance of rank odour, technically known as crude naphthalene or "naphthalene salts."

Crude Naphthalene.

To ascertain the quality of "naphthalene salts" an average sample of several kilograms is melted in a dish on the water-bath and thoroughly mixed. 15 to 20 grm. of the liquid is poured into a mortar and, after solidifying, broken into powder. 10 grm. are weighed on to filter-paper which is carefully folded over it, the whole being then enclosed in a piece of linen. The mass is then pressed in a small hydraulic press under a pressure of 200 atm. or in a vice till no more oil squeezes out. The solid cake is again powdered, the pressing being again repeated as before. The final cake obtained is weighed. A good sample of salts should not contain more than 10 to 12% of oil.

The proportion of higher hydrocarbons in the pressed cake is ascertained by distilling about 100 grm. (prepared as above) from a retort, the neck of which is kept warm so as to prevent it from becoming choked. A good sample of pressed salts should yield nothing below 210° and 90% should distil before 225° is reached.

The sublimed naphthalene of commerce contains 70 to 100% of the pure substance. The finer qualities form colourless crystals, but the inferior grades have a fawn or brown colour. A good test for the purity of sublimed naphthalene is to warm the sample in a test-tube with a little pure concentrated sulphuric acid. Pure naphthalene produces a colourless solution, but a decided pinkish tint is observed if as little as 1% of impurity is present. The colouration becomes deeper pink, or even brown, when a greater proportion of foreign matters is present.

The m. p. is always taken wet, as the difference between the m. p. of dry naphthalene and that containing a small amount of water is considerable, but the difference between that containing 4% of water and an amount in excess of this by several per cent. is inappreciable. So, unless it is known that the crude naphthalene contains as much as 4% of water, that much is added before taking the m. p.

The test is made after adding water in large brass or glass test-tubes, holding several ounces. The sample is melted and the point is noted when on cooling the temperature becomes constant after it has been rising. High m. p. naphthalenes show this constant temperature for quite a while. With low m. p. samples the point is not so sharply defined as the temperature does not remain constant very long. Those

not accustomed to making this test should repeat it until they feel sure that they have caught the point at which the temperature is constant for a longer or shorter time.

Water and so-called available naphthalene are estimated by distillation. 10 grm. are weighed into a small copper still connected with a condenser, a little heavy coal-tar naphtha (free from tar) is added and distillation begun. The distillation is carried to 205° (for carrying over water) with a water condenser and then it is completed with an air condenser. The distillation is carried to dryness. The residue left in the still is tarry matter and dirt. The percentage of water is added to this figure and the combined amount deducted from the amount of the original crude naphthalene taken, the balance being naphthalene available for refining. This is not all flake naphthalene as there is some oil present.

Refined naphthalene is valued by colour, m. p., a sulphuric acid test, and sometimes by distillation. The m. p. of naphthalene is generally between 78° and 78.5° (wet) and sometimes as high as 79°. Good results are not usually obtainable when the m. p. is so low as 78°.

The **sulphuric acid** test is a fairly sure indication of the keeping qualities as regards colour. The sample is melted and agitated with 1/3 volume of concentrated sulphuric acid for a short time. The naphthalene should remain white when first cooled. On remelting it generally becomes red. The acid is red in any case. If poorly refined the naphthalene will show yellowish to reddish and such material would not retain its colour.

The works' tests on crude and refined naphthalenes in the United States may show some differences from English and Continental practice. The above information is supplied by Mr. John M. Weiss, of Philadelphia.

Pure Naphthalene.

Specially purified naphthalene is now required in chemical industry particularly in the manufacture of azo-dyes. For this class of work naphthalene (dry) must melt sharply at 79°, boil between 217° and 218°, and be practically odourless; it must dissolve completely in light petroleum, giving a transparent, colourless solution. The monosulphonic acid prepared from it should not show a greyish tinge and the sodium salt of the acid must be snow-white. Naphthalene which answers these

requirements does not become yellow when exposed to air and light, and when dissolved in concentrated colourless sulphuric acid gives a solution with only a very faint pink colour.

The sensitiveness of naphthalene to air and light may be tested in the following way (Lunge's *Chem Tech. Unters. Meth.*, 1905, II, 762). A sample is left in a clock glass under a bell-shade over a vessel of pure, concentrated non-fuming nitric acid, when it should not show a yellow tinge for at least 1 or 2 hours. After this time even pure naphthalene changes colour owing to its undergoing nitration on the surface.

To test for phenol in naphthalene the latter is extracted with dilute sodium hydroxide solution, excess of hydrochloric acid added to the extract, and, after filtering, bromine water. Tribromophenol separates if phenol is present.

Basic substances are seldom found in naphthalene, but they can be detected, if present, by extracting with sulphuric acid, adding an excess of alkali and distilling with steam. The bases are recognised by their characteristic odour.

To estimate the percentage of naphthalene in a commercial product Küster (*Ber.*, 1894, **27**, 1101) devised the method of precipitation with picric acid. The procedure is that described on pages 245 and 276. The picrate may be either weighed or estimated volumetrically, using an excess of picric acid and titrating back. It is essential in this method that other hydrocarbons which form insoluble picrates should be absent.

NAPHTHALENE OILS.

This name, as also that of "creosote oil," is applied to the fraction of coal-tar distilling between 200° and 280° or 300°. Its composition is very imperfectly understood, but besides phenols and phenolic substances and a variety of bases, it is apparently largely composed of naphthalene and certain hydrides and homologues of that compound, the following of which have been described as being present.

Naphthalene dihydride, $C_{10}H_8H_2$, is a viscid liquid of strong, disagreeable smell, boiling at 200° to 210°. It is powerfully acted on by bromine, and is soluble in cold fuming nitric acid.

Naphthalene tetrahydride, $C_{10}H_8H_4$, resembles the dihydride, but boils at 190°.

α- and β-**Methylnaphthalenes,** $C_{10}H_7CH_3$, occur in the frac-

tion of coal-tar distilling between 220° and 270° (see Wendt, *J. Pr. Chem.*, ii, 1892, **46**, 317). At the ordinary temperature the α-variety forms a colourless liquid with a blue fluorescence and pleasant aromatic odour. It has a sp. gr. 1.0005 at 19°, distils in a current of open steam, boils at 240° to 243°, and crystallises at —22° to a hard mass. The *picrate* melts at 115.5°. α-Methylnaphthalene is miscible in all proportions with alcohol, ether, glacial acetic acid, carbon disulphide, and benzene. It is readily attacked by oxidising agents. β-Methylnaphthalene crystallises, like naphthalene, in large white plates, melts at 32.5°, and boils at 241 to 242°. Regarding the occurrence of α- and β-methylnaphthalenes in paraffin (Erdöl), see Tammann, D. R. P., 95579.

Dimethylnaphthalenes, $C_{10}H_6(CH_3)_2$. According to Emmert and Reingruber (*Annalen*, 1882, **211**, 365), the fraction of coal-tar boiling between 252° and 270°—after removing basic, oxygenated, and crystallisable substances—apparently consists of a mixture of several isomeric dimethylnaphthalenes, the separation of which has hitherto proved unmanageable. These compounds are said to constitute the major portion of coal-tar creosote oils.

The assay of naphthalene oils is described in the section on "Creosote Oils."

NAPHTHALENESULPHONIC ACIDS.
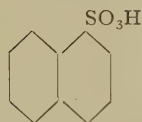
α-Naphthalenesulphonic acid.   β-Naphthalenesulphonic acid.

When naphthalene is heated with concentrated sulphuric acid α- and β-naphthalenesulphonic acids are formed. At low temperatures (80°) the α-acid is the principal product, but at higher temperatures (160° to 170°) and especially when an excess of sulphuric acid is present the β-acid predominates. When the α-acid is heated with concentrated sulphuric acid it is converted into the β-acid. Both acids are deliquescent, crystalline substances. They can be separated by the crystallisation of their calcium or lead salts, the α-salt having a very different solubility from that of the β-salt.

Differences:

α-Acid	β-Acid
Heated with hydrochloric acid at 200° gives naphthalene and sulphuric acid.	Heated with hydrochloric acid at 200° is not decomposed.
Sulphochloride, m. p. 66°, b. p. 195° (13 mm.).	Sulphochloride, m. p. 76°, b. p. 201° (13 mm.).
Sulphonamide, m. p. 150°	Sulphonamide, m. p. 212° (217° Corr.).

Numerous naphthalenedisulphonic and trisulphonic acids are known; for references see Reverdin and Fulda's *Tabellarische Uebersicht.*

NAPHTHOLS.

α–Naphthol.   β–Naphthol.
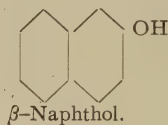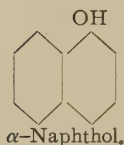
α- and β-naphthols (1- and 2-hydroxynaphthalenes) are prepared by fusing the corresponding α- and β-naphthalenesulphonic acids or their sodium salts with sodium hydroxide and subsequently liberating by dilute acid the naphthols from the sodium salts thus formed. They are of great importance in chemical industry as the starting-point from which a large number of important dyes are prepared. Both naphthols have been found in the "green oils" left after the filtration of the anthracene from a high boiling fraction of coal-tar (Schulze, *Annalen*, 1885, **227**, 143).

The naphthols are sparingly soluble in hot water (the α-compound less than the β-form) and nearly insoluble in cold water. They are easily soluble in most of the usual organic solvents. α-naphthol is far more volatile with steam than β-naphthol. Both naphthols—like phenols in general—are readily soluble in aqueous sodium hydroxide, forming sodium naphthoxides, which are decomposed by carbon dioxide, the parent naphthols being liberated. Aqueous solutions of

the naphthoxides on concentration undergo partial decomposition in the same manner. α- and β-naphthols are not soluble in solutions of alkali carbonates, but the nitronaphthols which are more acid in character, liberate carbon dioxide from carbonates forming salts analogous to the picrates.

With sulphuric acid the naphthols combine to form an important series of sulphonic acids. Nitric acid does not nitrate the naphthols in a simple manner[1] so that the nitronaphthols are generally prepared by indirect methods from the nitroso-naphthols or from naphthylamine-sulphonic acids (see Vol. 5). With bromine and chlorine the naphthols give a remarkable series of derivatives. The chlorine derivatives have been studied by Zincke: in this case the action is more complex than simple substitution, but with bromine simple substitution alone occurs, and a very large number of well-defined bromo-compounds can be isolated, the nature of the compound formed depending on the conditions (Davis, Reports of the British Association Committee, 1901 and 1902). Etherification is effected much more readily in the case of α- and β-naphthol than with most other phenols. On simply heating the naphthols with the corresponding alcohol and a small proportion of sulphuric acid the methyl- and ethyl-ethers are obtained in nearly theoretical proportion. The substituted naphthols etherify far less readily than the parent naphthols, in some cases not at all under the conditions named (see Davis, Trans., 1900, 77, 33).

Qualitative Tests.—The analytical examination of the naphthols has become of importance in view of their value as antiseptics, disinfectants, and therapeutic agents. β-naphthol is now almost exclusively used, being regarded as the less toxic form. It is now readily obtainable in a high degree of purity. Many tests have been devised for distinguishing between the two naphthols and for detecting one in the presence of the other. The following table summarises the more trustworthy of these, as applied to the purified substances:

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[1] When β-naphthol is carefully nitrated with the theoretical quantity of nitric acid in glacial acetic acid solution at 0° and the product then treated with sodium sulphite solution (to reduce the nitro keto-compound initially formed) about 50% of the theoretical quantity of 1-nitro-2-naphthol is obtained on steaming (Davis). When α- and β-naphthols are exposed to the action of nitrogen dioxide (NO_2) and the products treated with alkalies or, better, with alkaline sulphite, mononitro-derivatives of the naphthols are obtained (Armstrong and Rossiter, Proc., 1891, 7, 91).

	α-Naphthol	β-Naphthol
Odour	Faint, resembling phenol.	Almost odourless.
Crystalline form	Monoclinic needles ..	Monoclinic plates.
M. p., °	94	122
B. p., °	280. Readily distils with open steam.	286. Scarcely distils with open steam.
Ferric chloride in aqueous solution.	Red, turning to violet.	Pale green.
Bleaching powder in aqueous solution.	Dark violet, changing to reddish-brown.	Pale yellow. When excess of bleaching powder is present, the colour disappears
Azo-test, 1 c.c. of acid solution of sulphanilic acid (sulphanilic acid, 0.5 grm.; acetic acid [30%], 150 c.c.). Freshly prepared very dilute solution of sodium nitrite, a few drops added at time of making test. The colours develop slowly.	Orange-red	Yellow.
A few drops of a solution of 1 grm. of potassium dichromate and 1 grm. of nitric acid in 100 c.c. of distilled water, added to a solution of the sample in water or very dilute alcohol.	Black precipitate ...	No precipitate.
0.1 grm. of vanillin is dissolved in 2 c.c. sulphuric acid and 0.1 grm. of naphthol added and the mixture shaken.	Permanent red colour.	Green solution.

For distinguishing between *naphthalene, α-naphthol,* and *β-naphthol,* L. Reuter (*Pharm. Zeit.,* 1891, 289) utilises the difference of action of chloral hydrate and zinc. 0.1 grm. of the sample is mixed with 2.5 grm. of fused chloral hydrate and warmed for ten minutes. A similar experiment is performed with addition of 5 drops of strong hydrochloric acid, and also with the same amount of acid and a piece of zinc.

Jorissen (*Ann. Chim. Anal.,* 1902, **7,** 217) recommends as a means of distinguishing α-naphthol from β-naphthol the following procedure: A pinch of the sample is mixed in a test-tube with 2 c.c. of a solution of iodine in potassium iodide and then with an excess of aqueous sodium hydroxide. On shaking, β-naphthol gives a clear, colourless liquid, but α-naphthol gives a turbid liquid of an intensely violet colour. In the case of a mixture the colour is proportional to the amount of α-naphthol present.

	Naphthalene	α-Naphthol	β-Naphthol
Chloral hydrate ..	Colourless....	Intensely ruby-r e d, transparent, not fluorescent.	Pure blue, transparent, not fluorescent.
Chloral hydrate, and acid.	Very slight pink.	Intensely dark greenish-blue, not transparent.	Intensely y e l l o w, transparent.
Chloral hydrate, acid and zinc.	Violet, passing into brown.	A dark violet-blue. (Water gives a violet flocculent precipitate.) Alcoholic solution, reddish-violet with a violet fluorescence.	Dark brown. (Water t h r o w s down a greasy ppt.) Alcoholic solution, yellow with a blue fluorescence.

Commercial α-naphthol.

The best means of ascertaining the degree of purity of either of the commercially pure naphthols is to take the m. p. Technical α-naphthol generally consists of crystalline lumps formed by the solidification of the fused material and melts somewhat below 94°, the m. p. of the pure naphthol, owing to the presence of small quantities of β-naphthol as an impurity. o.5 grm. of the naphthol when ignited should not leave behind any weighable ash. As in the case of β-naphthol, α-naphthol should dissolve completely in aqueous ammonia (sp. gr. o.96) (absence of naphthalene).

Commercial β-naphthol.

Technical β-naphthol is usually a highly purified substance, and should melt at 122°. The U. S. P. requirements are that it should leave no ash and that 1 grm. should dissolve completely in 50 c.c. of ammonia (sp. gr. o.96) (absence of naphthalene)—the solution having only a pale yellow colour (absence of organic impurities). On shaking 1 grm. of the naphthol with 100 c.c. of water the solution should be neutral to litmus-paper (absence of organic acids). On dissolving 1 grm. of β-naphthol in boiling water (100 c.c.) filtering and adding bleaching powder, the solution should show only a pale yellow and not a violet colour (absence of α-naphthol).

To detect α-naphthol in β-naphthol Jorissen's test (see above) may also be used.

For the quantitative estimation of α-naphthol in presence of large proportions of β-naphthol, J. Prochazka and H. N. Herman[1] have devised the following process, depending on the greater facility with which α-naphthol combines with diazo-compounds:

27.5 grm. of 90% sodium naphthionate are dissolved in 185 c.c. of water. 6.2 c.c. of sulphuric acid (sp. gr. 1.835) are diluted with 180 c.c. of water and the mixture run slowly into the naphthionate solution, which is continuously stirred to secure a uniform paste. The mixture is cooled to below 5°, and a 10% solution of sodium nitrite, containing 7 grm. of the commercial 98% product, added slowly, stirring constantly. The resulting paste, made up to 750 c.c., is now ready for use.

For the test, 15 grm. of the sample, 200 grm. of a 25% solution of sodium hydroxide solution, and 140 c.c. of a 10% solution of sodium carbonate are heated together until the β-naphthol is dissolved. The solution is cooled to below 5° and made up at 250 c.c. The diazo-compound as prepared is run slowly and carefully into this solution of the sample, which is continually stirred. If the β-naphthol is pure, the resulting azo-compound will precipitate completely in the shape of a fine crystalline powder, and hardly any colour will pass into solution; while the first portions of the diazo-compound are being added. On the contrary, if α-naphthol is present, a coloured solution will be formed. As little as 0.1% can be detected. If the rest of the diazo-compound be added, the presence of the α-naphthol compound is obscured by the formation of a thick colour paste. However, by boiling the product the paste is made to settle as a layer of fine crystals, and the supernatant liquid is more or less coloured with the α-naphthol compound. The following short method may be used: Instead of combining the whole of the β-naphthol, only a part—say, 5% of the whole—is combined with diazo-compound. The diazo-paste prepared as above is well shaken and 37.5 c.c. run into the β-naphthol solution of the same quantity as above, and with the same precautions as already described. It is then not necessary to boil the product, as the insoluble dyestuff formed settles readily, and by dipping strips of filtering paper into the supernatant liquid, and comparing the tint with that obtained similarly from mixtures of pure β-naphthol with a known percentage of α-naphthol, a fairly accurate idea of the amount of α-naphthol present can be obtained. The method can be further

[1] J. Soc. Chem. Ind., 1897 16, 894.

simplified by using colour solutions of known strength and same shade as that of the above coloured filtrate, for the purpose of comparison. With proper caution the method can be successfully applied to less than 1 grm. A somewhat similar method, using diazotised *p*-nitraniline has been devised by Liebmann (*J. Soc. Chem. Ind.*, 1897, **16**, 294). In this paper the purification of β-naphthol is also described. The test is as follows:

0.144 grm. of the naphthol is dissolved in 5 c.c. of pure alcohol in a graduated cylinder and 15 c.c. of toluene added. 0.14 grm. of *p*-nitraniline is dissolved in 9 c.c. of dilute hydrochloric acid and diazotised, after thoroughly cooling in a freezing mixture, with 1 c.c. of normal sodium nitrite solution. The diazo solution is poured into the naphthol solution, some water added, and the mixture, shaken and allowed to separate into two layers in a separating funnel. The toluene layer is shaken with 5 c.c. of sodium hydroxide solution and the colour of the liquid compared with that of solutions of β-naphthol made in a similar way from β-naphthol containing known proportions of α-naphthol. These solutions must be freshly prepared, as the colour changes on keeping. This test allows of the estimation of such small quantities of α-naphthol as 0.01 grm.

Detection of β-naphthol in Foods.—The marked antiseptic qualities of β-naphthol render it suitable for use as a food-preservative but it has not been largely employed. For its detection in ordinary foods, the American Association of Official Agricultural Chemists suggested the following procedure, which covers also the detection of several similar antiseptics (Proc. 14th Ann. Conv., 1897, *A. O. A. C.*, Bull. 51, *U. S. Dept., of Agric.*).

200 grm. of the sample are acidified with dilute sulphuric acid, distilled with open steam, and the first 200 c.c. of the distillate extracted in a separating funnel with about 20 c.c. of chloroform. After being run off, the chloroform is rendered slightly alkaline with potassium hydroxide and heated for a few minutes almost to boiling. Colour changes occur as follows, if an antiseptic of the phenol class is present:

Phenol............Light red, to brown, to yellow, to colourless.
o-Cresol...........Lilac with tinge of orange.
β-naphthol ....Deep blue, to green, to brown.
Salol ....Light red.

In Bulletin No. 107 (1907) the procedure recommended is as follows: Extract 200 c.c. of the sample (or of its aqueous extract prepared

by macerating 200 to 300 grm. of the sample with water made slightly alkaline with sodium hydroxide and straining through a cotton bag) with 10 c.c. of chloroform in a separating funnel, add a few drops of alcoholic potassium hydroxide to the chloroform extract and place on a boiling water-bath during 2 minutes. The presence of β-naphthol is indicated by the formation of a deep blue colour which changes through green to yellow.

Estimation of β-Naphthol.—This is seldom necessary as the best method of ascertaining the degree of purity of a sample of the commercial article is by means of the m. p. and the qualitative tests already given. The methods that have been suggested for estimating β-naphthol, which will be briefly indicated, are only reliable when applied to the pure substance. Thus, in the picric acid method, α-naphthol, naphthalene, and other hydrocarbons are returned as β-naphthol. If the iodometric method is used. other substances. such as phenols are generally present which absorb iodine; α-naphthol, for instance, counts as β-naphthol.

1. **Picric Acid Method.**—This is carried out by Küster (*Ber.*, 1894, **27**, 1101) exactly as in estimating naphthalene (pp. 245 and 276) by means of picric acid. A weighed quantity of the substance is digested in a sealed flask (preferably under reduced pressure) on the water-bath, with a measured volume of a saturated aqueous solution of picric acid. The naphthol is converted quantitatively into an insoluble picrate, and the amount of picric acid remaining in solution is ascertained by titration of an aliquot portion with $N/10$ barium hydroxide (see under *Naphthalene*). As β-naphthol picrate is slightly soluble in water, it is necessary to allow 0.0075 grm. of β-naphthol per 100 c.c. of picric acid solution used, this being the quantity which remains in solution at the ordinary temperature.

2. **Iodometric Method** (Messinger and Vortmann, *Ber.*, 1890, **23**, 2754).—3 grm. of the sample are dissolved in a solution of not less than 3,5 grm. of sodium hydroxide ($= C_{10}H_7HO + 4NaHO$), and the solution diluted to an exact volume, not less than 250 c.c. Ten c.c. of the solution are placed in a small flask, heated to 55°, and $N/10$ iodine solution added until the liquid shows a yellow colour, indicating excess of iodine. On shaking, a dirty green precipitate may be produced. The liquid is cooled, acidified with sulphuric acid, diluted to 250 c.c., and an aliquot portion titrated with decinormal sodium thiosulphate to ascertain the excess of iodine. The figure for the

iodine actually used, calculated to the whole amount taken, and multiplied by 0.3784, will give the amount of β-naphthol present.

As the degree of action of the iodine varies with the concentration of the β-naphthol solution, Küster (*Ber.*, 1894, **27,** 1905) gives a table of corrections to be introduced for different concentrations.

As stated above, Messinger and Vortmann's method is a general method for phenols, and is useless for β-naphthol in presence of such substances as phenol, cresols, salicylic acid, thymol, etc.

β-NAPHTHOL ETHERS.

β-**Naphthol Methyl Ether** (*β-Methoxynaphthalene*) crystallises from light petroleum in small leaflets, m. p. 72°, b. p. 274°. It is used in perfumery under the name *Yara-Yara*.

β-**Naphthol Ethyl Ether** (*β-Ethoxynaphthalene*), m. p. 37°, b. p. 274–275°, crystallises in large plates from light petroleum. It is used in perfumery under the name *nerolin*, which is also applied to β-methoxynaphthalene.

β-NAPHTHOLSULPHONIC ACIDS.

Those sulphonic acids of β-naphthol which are of importance in dyeing will be dealt with in Vol. 5.

Abrastol or asaprol is calcium β-naphtholsulphonate, $(OH.C_{10}H_6SO_3)_2Ca$. For detecting this substance, Bulletin No. 107 (1907) of the U. S. Dept. of Agriculture, Bureau of Chemistry, gives the following tests (see also page 401).

1. **Sinabaldi's Test.**—Make 50 c.c. of the sample alkaline with a few drops of ammonia and extract with 10 c.c. of amyl alcohol (ethyl alcohol is added if an emulsion is formed). Decant the amyl alcohol, filter if turbid, and evaporate to dryness. Add to the residue 2 c.c. of a mixture of equal parts of conc. nitric acid and water, heat on a water-bath until half the water has evaporated and transfer to a test-tube adding 1 c.c. of water. Then add about 0.2 c.c. of ferrous sulphate solution and an excess of ammonia drop by drop, shaking continuously. If the precipitate is reddish in colour, dissolve it in a few drops of sulphuric acid and add ferrous sulphate and ammonia as before. As soon as a dark coloured or greenish precipitate has been obtained, introduce 5 c.c. of alcohol, dissolve the precipitate in

sulphuric acid, shake well and filter.   When abrastol is absent this
method gives a colourless or light yellow liquid, while a red colour is
produced when abrastol is present to the extent of 0.01 grm.

2. **Sanglé-Ferrière's Method.**—Boil 200 c.c. of the sample with
8 c.c. of concentrated hydrochloric acid during one hour beneath a
reflux apparatus.   Abrastol is converted in β-naphthol which can be
detected by the method given on page 257.

Leffmann gives the following test for the presence of abrastol in
milk.   To 10 c.c. add 0.5 c.c. of mercuric nitrate solution made by
dissolving mercury in twice its weight of nitric acid and diluting with
5 vols. of water.   If abrastol is present a yellow colouration rapidly
appears.   In testing wines, acidify with a few drops of dilute sul-
phuric acid and shake with an equal volume of chloroform or ether.
To the chloroform or ethereal layer, a few drops of mercuric nitrate
solution is added and the mixture shaken.   If abrastol is present the
mercury solution turns yellow and finally red.   If a fat is examined it
should be melted and the abrastol removed by shaking with 20%
alcohol.   The alcohol is removed by distillation and the residual
aqueous solution is tested with the mercury solution as above.

NITRONAPHTHALENES.

The nitronaphthalenes, especially α-nitronaphthalene, are of im-
portance in connection with explosives (see p. 559) as their presence
renders nitroglycerin non-sensitive to concussion; when present,
even in very small proportion, they prevent dynamite from freezing.
They considerably increase the solvent action of nitroglycerin on
nitrocellulose.

α-Nitronaphthalene is also of importance as the material from
which α-naphthylamine is prepared.   It forms pale yellow needles,
is easily soluble in alcohol and ether, insoluble in water, m. p. 61°, b. p.
394°.   The m. p. is the test of purity of the commercial article.

ANTHRACENE AND ITS ASSOCIATES.

By S. S. SADTLER.

In the distillation of coal-tar, the fraction passing over above the temperature of 270° is a heavy, greenish or reddish, oily liquid known as anthracene oil, which usually amounts to about 1/6 of the entire distillate. In the case of water-gas tar the anthracene oil is similar to that from coal-tar, but contains less crystallisable anthracene. On cooling completely, a granular, crystalline deposit is formed, which consists chiefly of a mixture of various solid hydrocarbons, of which anthracene is the most important and characteristic. The deposit is freed as much as possible from the adherent oil by filtration, pressure, or other mechanical means. Formerly it was sold in a pasty state, but the purification is now carried further. To obtain a superior product it is desirable to use powerful hydraulic pressure, and to press the crude anthracene, first cold and then hot, by which means a 30 to 40% cake may be obtained without washing. The anthracene may be further purified by treatment, after crushing, with coal-tar naphtha boiling between 120° and 190°, which, in some cases, is subsequently washed out by petroleum spirit boiling between 70° and 90°.[1] Anthracene and the other chief constituents of the product thus obtained are described in the following sections. The assay of the crude anthracene is described on page 282, *et seq.*

Anthracene. $C_{14}H_{10} =$
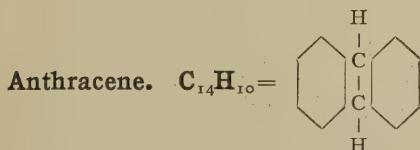
Anthracene is formed in a variety of reactions taking place at high temperatures. It is a characteristic constituent of coal-tar from the

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[1] The solvent is recovered by distillation. The residue consists largely of phenanthrene and liquid oils of unknown nature. It has been used for making lamp-black and mixed with other oils for use in creosoting.

manufacture of illuminating gas, and is also found in the tar produced by condensing the gas from by-product coke-ovens and in the tar obtained in the manufacture of gas by exposing petroleum to a high temperature as in carburetted water-gas. Anthracene is now manufactured on a large scale from the high-boiling fractions of these tars (see above). It is contained in notable quantity in coal-tar pitch, and hence the distillation of this product has been carried as far as actual coking in order to obtain the greatest possible yield of anthracene, but the product was so impure, and is refined with such difficulty, that the manufacture from this source has been abandoned. In the United States and in other countries where coal-tar dye stuffs are not manufactured to any extent, anthracene is not separated and is included in in the creosote used for impregnating wood.

When quite pure, anthracene crystallises in colourless rhomboidal plates or shining scales, which exhibit a fine violet fluorescence. It melts at 213°, sublimes at about the same temperature in micaceous scales, and distils almost unchanged at about 360°.[1] It may be distilled nearly unchanged in admixture with potassium hydroxide and Perkin recommended this as the only method by which crude anthracene could be purified on the large scale.

Anthracene is insoluble in water, and in dilute acid and alkaline solutions. In cold alcohol chemically pure anthracene dissolves to the extent of 0.6% while benzene dissolves 0.9 and carbon disulphide 1.7% of anthracene.

If picric acid be added to a solution of anthracene in boiling benzene, a compound having the formula $C_{14}H_{10}$, $C_6H_2(NO_2)_3OH$ is formed. On cooling, this so-called picrate separates in ruby-red needles, which melt at 170°, and are soluble in a small proportion of alcohol with red colour, but on adding more alcohol the compound undergoes decomposition and the liquid is decolourised. The crystals are also decomposed by water.

Hot dilute nitric acid converts anthracene into a mixture of anthraquinone with dinitroanthraquinone, $C_{14}H_6(NO_2)_2O_2$. The latter substance crystallises in microscopic quadratic plates, and, according to Fritzsche, forms compounds with all the solid hydrocarbons associated with anthracene in coal-tar. With anthracene itself, Fritzsche's reagent gives shining, rhomboidal, purple plates, which appear blue

[1] Nearly pure anthracene may be obtained by melting a partially purified sample in a retort and passing a strong current of air through it, when the anthracene is carried off and deposited in brilliant flakes.

if the hydrocarbon be not quite pure; and if too impure, the reaction fails altogether.

On gently heating, concentrated sulphuric acid dissolves anthracene with greenish colour, and at a higher temperature forms anthracene sulphonic acids. Fuming sulphuric acid acts violently on anthracene.

By the action of bromine or chlorine, anthracene is converted into various bromo- and chloro-derivatives. On treating dibromanthracene, $C_{14}H_8Br_2$, with oxidising agents, it is converted into dibromanthraquinone, $C_{14}H_6Br_2O_2$, and this, when heated with potassium hydroxide, yields dihydroxyanthraquinone or alizarin, $C_{14}H_6(OH)_2O_2$. Similarly, by treatment with chlorine, anthracene is converted into the theoretical weight of dichloranthracene, $C_{14}H_8Cl_2$, a lemon-yellow crystalline substance resembling picric acid. The reaction forms an important step in the manufacture of artificial alizarin.

By exposing purified anthracene suspended in benzene or xylene to the action of direct sunlight for several weeks a modification, formerly called *paranthracene*, is obtained, but which Orndorff and Cameron[1] found to have the formula $C_{28}H_{20}$, and propose the name *dianthracene*. It has a sp. gr. of 1.265 $\left(\frac{27°}{4°}\right)$. It melts at 244°. It differs from anthracene in many points. It is not soluble in benzene, is not attacked by ordinary nitric acid or bromine, and does not combine with picric acid. It is converted into anthraquinone by chromic acid or warm fuming nitric acid.

Anthraquinone. $C_{14}H_8O_2 =$
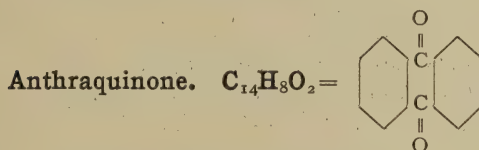
Anthraquinone has the constitution of a diphenylene-diketone. It is produced by the action of oxidising agents on anthracene. Chromic acid is the best oxidiser for the purpose; with nitric acid, nitranthraquinone is apt to be produced. The details of the process are given on page 282 *et seq.*

As usually prepared, anthraquinone appears as a felted mass of delicate crystalline needles of a yellowish or pale buff colour, but when purified by sublimation, it is obtained in long, delicate, lemon-yellow needles, or golden-yellow prisms. When pure, it melts at

[1] *Amer. Chem. Jour.*, 1895, 658.

277°, and boils at a temperature between the points of ebullition of mercury and sulphur (over 360°).

Anthraquinone is neutral in reaction, and insoluble in water and in dilute acid and alkaline liquids.   It is sparingly soluble in alcohol and ether; more soluble in hot benzene.   It is very stable, resisting the action of many reagents.   It is not affected by hot hydrochloric acid, or by boiling with solution of potassium hydroxide or calcium hydroxide.   It dissolves in hot nitric acid of 1.4 sp. gr., and is deposited in crystals on cooling,—a more complete separation occurring when the acid is diluted.

In concentrated sulphuric acid at 100° anthraquinone dissolves unchanged, and on exposing the solution to a moist atmosphere, is gradually redeposited in crystals, or may be obtained in a more finely-divided state by pouring the acid into water.   Solution in sulphuric acid is employed for purifying commercial anthraquinone. When strongly heated with concentrated sulphuric acid, or more easily if fuming acid be used, entirely or in part with 66° acid, anthraquinone is converted into a mixture of anthraquinone monosulphonic and anthraquinone-disulphonic acid.   These bodies are also obtained by the action of sulphuric acid on dichloranthracene, $C_{14}H_8Cl_2$, and play an important part in the manufacture of artificial alizarin.   The proportion of the 2 sulphonic acids formed depends on that of the sulphuric acid employed.   On nearly neutralising the product with sodium hydroxide, sparingly soluble sodium anthraquinone-monosulphonate separates, and may be obtained in brilliant pearly scales by pressure and recrystallisation.   Heated with sodium hydroxide and potassium chlorate it yields pure alizarin.

When fused with potassium hydroxide, anthraquinone yields potassium benzoate, and when ignited with or distilled over soda-lime, benzene is formed.

By the action of certain reducing agents, such as sodium amalgam or sodium hydroxide solution and zinc dust, anthraquinone is converted into hydranthraquinone, $C_{14}H_{10}O_2$.   This reaction has been applied by A. Claus as an extremely delicate means of detecting anthraquinone, and hence anthracene.   A few particles should be placed in a test-tube with some sodium amalgam, covered with ether free from water and alcohol, and the whole well shaken together.   On adding a drop of water a splendid red colour appears, but is destroyed by shaking in contact with air, reappearing on standing.   If absolute alcohol

be substituted for the ether, the colour produced is dark green, turned to red by a trace of water, and destroyed by shaking with air.

The marked characters and stability of anthraquinone render it the most convenient body into which to convert anthracene for the purpose of estimating it. The best method of effecting this is described on page 282.

Anthracene Dihydride, $C_{14}H_{12} = C_{14}H_{10} . H_2$, occurs in coal-tar. It crystallises in colourless plates resembling naphthalene, fuses at 106°, and distils unchanged at 305°. It has a peculiar odour, sublimes at the temperature of boiling water, and distils readily with the vapour of water or alcohol. Anthracene dihydride is insoluble in water, but is readily soluble in alcohol, ether, or benzene, the solutions exhibiting a blue fluorescence, which is not shown by the solid substance. It is said not to yield a compound with picric acid.

Anthracene Hexahydride, $C_{14}H_{16} = C_{14}H_{10}H_6$, occurs in coal-tar with the dihydride, which it closely resembles. It melts at 63° and boils at 290°.
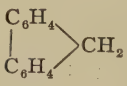
Methylanthracene, $C_{15}H_{12} = C_{14}H_9(CH_3)$, occurs in small quantities in coal-tar, and is produced by the reduction of chrysophanic acid and other bodies. It resembles anthracene, crystallises from hot alcohol in thin, pale yellow, bright scales, and sublimes in greenish scales. It melts at a temperature variously stated at 200° to 210°, is sparingly soluble in alcohol, ether, and glacial acetic acid, but readily in benzene, chloroform, and carbon disulphide. It forms a picric acid compound similar to that of anthracene, and is dissolved by concentrated nitric or sulphuric acid, especially if hot.
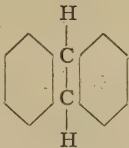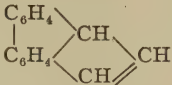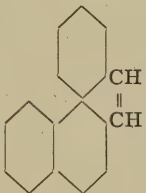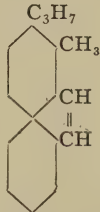
Dimethylanthracene, $C_{16}H_{14} = C_{14}H_8(CH_3)_2$, resembles the last compound, melts at 224° to 225° and is supposed, though not proved, to exist in coal-tar.

CONSTITUENTS OF CRUDE ANTHRACENE.

The crude commercial anthracene, obtained from coal-tar in the manner described in outline on page 23, is an extremely complex mixture of hydrocarbons and other organic compounds, some of which have been but very imperfectly studied. The tables on pages 266 and 267 give a synopsis of the principal hydrocarbons occurring in crude anthracene:[1]

[1] The structural formulæ have been compiled principally from the last (8th) German edition of Richter's *Organic Chemistry*, which gives for retene merely the general structure, as a methylpropylphenanthrene. In the formula for retene, given in the table, the assignment of the alkyls to particular points is merely provisional.

Name	Empirical formula	Structural formula	M. p., °	B. p., °
Naphthalene	$C_{10}H_8$		79	218
Diphenyl	$C_{12}H_{10}$		70.5	254
Acenaphthene	$C_{12}H_{10}$	$H_2C\!-\!\!-\!CH_2$	95	277.5
Diphenylmethane	$C_{13}H_{12}$	HCH	26	262
Fluorene...................	$C_{13}H_{10}$	C_6H_4 $>CH_2$ C_6H_4	113	295
Phenanthrene..............	$C_{14}H_{10}$	CH ‖ CH	96	340

Name	Empirical formula	Structural formula	M. p., °	B. p., °
Anthracene...................	$C_{14}H_{10}$	H C C H (hexagon rings)	213	360
Fluoranthene...............	$C_{15}H_{10}$	C_6H_4 CH C_6H_4 CH CH	109	360+
Pyrene....................	$C_{16}H_{10}$	(fused ring structure)	148	371
Chrysene..................	$C_{18}H_{12}$	CH ‖ CH	248	436
Retene (methylisopropylphen-anthrene)...............	$C_{18}H_{18}$	C_3H_7 CH$_3$ CH ‖ CH	98	390

Besides the bodies classified in the foregoing table, and methyl-anthracene and the hydrogen additive compounds of anthracene already described, crude anthracene is apt to contain other hydro-carbons of which but little is known. A solid paraffin is present in considerable quantity in the crude anthracene made from the tar of cannel coal.

Crude commercial anthracene also contains liquid hydrocarbons of high b. p. and almost unknown composition; the phenols corre-sponding to anthracene, phenanthrene, and probably to other hydro-carbons; and the nitrogenised bodies carbazol, imido-phenylnaphthyl, and acridine.

The following is a more detailed description of the principal bodies occurring in association with anthracene in the crude commercial product. Some of their important reactions are described on page 273 *et seq.:*

Naphthalene, $C_{10}H_8$, has already been fully described. It can be separated from crude anthracene with tolerable facility, as it is taken up by solvents more readily than are the associated hydrocarbons, and has a lower m. p. and b. p.

Diphenyl, $C_{12}H_{10}$, dissolves readily in alcohol and ether, and crys-tallises from its solutions in large, colourless scales. It may be isolated from the indifferent oils of the fraction of coal-tar boiling between 240° and 300° by treating them with warm sulphuric acid, sepa-rating the resultant mono- and dimethylnaphthalene-sulphonates, and cooling the undissolved oil to —15°, when the diphenyl sepa-rates out. Oxidation converts diphenyl into benzoic acid.

Acenaphthene, $C_{12}H_{10}$, is metameric with diphenyl. It occurs chiefly in the fraction of coal-tar distilling between 270° and 300°, and crystallises from the 280° to 290° fraction on cooling. It may be purified by crystallisation from hot alcohol or coal-tar naphtha, followed by careful sublimation. From alcohol it crystallises in long, colourless, lustrous needles, and from heavy tar oil in hard, brittle crysals. Ace-naphthene has an odour like that of naphthalene, is readily acted on by bromine, forms a sulphonic acid all the salts of which are readily soluble, and yields a nitro-compound with nitric acid.

Acenaphthene dihydride, $C_{12}H_{10}H_2$, is stated to occur in coal-tar and to boil at 260°

Diphenylmethane is crystalline and has an odour resembling orange peel. Oxidation with chromic acid converts it into benzophenone.

Fluorene, $C_{13}H_{10}$, is contained in the fraction of coal-tar boiling between 290° and 350°, and particularly in the 295–310° fraction, from which it may be isolated by repeated crystallisation from alcohol. Fluorene forms colourless, fluorescent scales, easily soluble in hot alcohol and in benzene, ether, and carbon disulphide. It yields derivatives with bromine and nitric acid.

Phenanthrene, $C_{14}H_{10}$, is metameric with anthracene, and occurs in the crude substance in very considerable proportion. It may be separated from anthracene by fractional distillation followed by repeated crystallisation from alcohol, in which liquid it is much more soluble than anthracene, and hence becomes concentrated, in the mother-liquors. It crystallises in colourless lustrous plates. The fusing-point of phenanthrene is much lower than that of anthracene, but it sublimes less readily than the latter hydrocarbon, though its b. p. is lower. It is also distinguished from anthracene by its behaviour with picric acid, with antimony and bismuth chlorides, and with chromic acid. Phenanthrene forms a sulphonic acid when heated to 100° with concentrated sulphuric acid, and with nitric acid yields a nitro-compound. Its behavior with chromic acid is described on page 278.

Pseudophenanthrene, $C_{16}H_{12}$, occurs in small quantity in the portion of crude anthracene soluble in acetic ether. It forms large, white, glistening plates, exhibiting no fluorescence, and melting at 150°. This last character distinguishes it from phenanthrene and similar hydrocarbons, as does the fact that the picrate separates on mixing cold saturated alcoholic solutions of the hydrocarbon and picric acid. It is also characterised by the properties of the product formed on oxidising it with chromic acid.

Fluoranthrene, or Idryl, $C_{15}H_{10}$, occurs in the highest-boiling fractions of coal-tar, and is best separated from the accompanying pyrene by repeated crystallisations of its picric acid compound from alcohol. Fluoranthrene crystallises from dilute alcohol in large shining plates, from strong alcohol in needles. It dissolves in concentrated sulphuric acid, on gently warming, with greenish-blue colouration, changing at a higher temperature to blue, and at length turning brown.

Pyrene, $C_{16}H_{10}$, is contained in the fractions of the oils of coal-tar and crude anthracene boiling above 360°. On extracting these with carbon disulphide, evaporating the filtered solution to dryness, dis-

solving the residue in hot alcohol, and adding an alcoholic solution of picric acid, the picrate separates on cooling. The compound should be recrystallised several times from alcohol, decomposed by ammonia, and the separated hydrocarbon recrystallised from alcohol. It forms colourless, tabular crystals.

Retene, $C_{18}H_{18}$, occurs in thin, unctuous scales in fossil pine-stems, in beds of peat and lignite; and is also produced in the dry distillation of very resinous fir and pine wood. It forms shining scales. Retene volatilises readily at 100° and slowly at the ordinary temperature, but is devoid of smell. It sinks in cold water and floats on boiling water.

Chrysene, $C_{18}H_{12}$, is contained in the fraction of coal-tar which distils immediately before the occurrence of coking, when it is obtained in admixture with pyrene as a dry powder or yellow mass. On extracting this with carbon disulphide chrysene remains, and may be purified by crystallisation from hot glacial acetic acid or heavy tar oil. Turpentine oil also dissolves it, but in carbon disulphide it is nearly insoluble. Chrysene forms brilliant scales, which when pure are colourless, but which are commonly obtained yellow, owing to the presence of chrysogene as a persistent impurity. Chrysene boils at about the same temperature as sulphur, with partial decomposition. It forms compounds with picric acid and dinitro-anthraquinone, yields nitro-compounds with nitric acid, and dissolves in hot, concentrated sulphuric acid with purple colour.

Chrysogene is the body which imparts to impure chrysene its yellow colour. Its formula has not been established. It is isolated from crude chrysene by frequent crystallisation from coal-tar naphtha, and washing with ether and alcohol. Chrysogene crystallises from boiling alcohol in yellow, cohering scales, which if very thin are pink, with a gold-green reflection. It dissolves in 2,500 of cold or 500 parts of boiling benzene, and in 10,000 of cold or 2,000 of boiling glacial acetic acid. The presence of 1/1000 part of chrysogene colors naphthalene and other hydrocarbons an intense yellow. Its solutions are rapidly decolourized on exposure to sunlight. Chrysogene fuses at 280–290° with partial decomposition, and dissolves without visible change in concentrated sulphuric acid.

Benzerythrene, or Triphenylbenzene, $C_{24}H_{18} = C_6H_3(C_6H_5)_3$. This hydrocarbon forms the very last product obtained in the distillation of coal-tar pitch, and may thus be separated without difficulty. After nearly all the other bodies have passed over, the benzerythrene

appears as a vapour easily condensing to a bright-red powder, which, however, contains much chrysene and other bodies troublesome to separate. When pure, it forms white, shining scales which melt at 207°, and are but sparingly soluble in alcohol, or even in boiling glacial acetic acid, but are more soluble in hot benzene. In strong sulphuric acid benzerythrene dissolves with green colour. The symmetric form has been obtained artificially.

Picene, or parachrysene, $C_{22}H_{14}$, resembles chrysene, but is still less acted on by solvents. Its best solvents is high-boiling coal-tar naphtha. Picene melts at an exceptionally high temperature (330–345°), and boils at 518–520°.

Paraffins, C_nH_{2n+2}. In the crude anthracene from the tar of cannel coal, such as is produced in Scotch and north-country gas works, a solid paraffin is present in considerable quantity and is a highly objectionable impurity, as it greatly reduces the value of the product and even renders some batches wholly unmarketable. It has been stated that water-gas tar creosote contains considerable quantities of paraffins, but the reviser has examined several samples by the sulphonation method described on page 384 and found less than in coal-tar and only a fraction of 1% based on the whole creosote fraction.

Carbazol. Imido-diphenyl. Diphenylene-imide.

$$C_{12}H_9N =$$
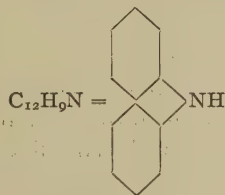
Carbazol often occurs in crude washed anthracene to the extent of 10 or 12%. It is best isolated from the residue left in the retort after purifying crude anthracene by distillation with potassium hydroxide. It exists in this as a potassium derivative, $C_{12}H_8NK$, which is decomposed by water with formation of potassium hydroxide and regeneration of the carbazol. Carbazol fuses at 238° C., sublimes readily, and boils at about 355°. It forms colourless, crystalline, fluorescent scales or plates, which resemble anthracene. It is insoluble in water, and but little dissolved by cold alcohol, ether, chloroform, or benzene, but more readily by these solvents when hot. It has no basic properties like acridine and forms no salts with acids, but substitution

products with potassium and with acetyl exist. Its characters are very similar to those of the hydrocarbons with which it is associated. Carbazol forms a compound with picric acid, and with nitric acid yields nitro-compounds. In pure cold sulphuric acid it dissolves with yellow colour, but in presence of the most minute trace of nitric acid, chlorine, chromic acid, or other oxidising agent, an intense green colouration is produced. It is employed for the preparation of several dye-stuffs. S. C. Hooker has suggested its use as a colorimetric test for nitrates in water.

PHENYLNAPHTHYLIMIDS. Phenylnaphthylamine

$$C_{16}H_{11}N =$$ —NH
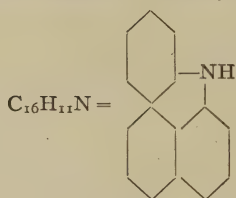
This body is obtained by subliming the residue remaining after distilling crude anthracene. It crystallises in greenish or golden-yellow metallic-looking plates, melts when pure at 330°, and boils at a higher temperature than sulphur. It is but little soluble in alcohol, benzene, toluene, or glacial acetic acid, even when boiling, and with difficulty in high-boiling coal-tar naphtha. It is more soluble in hot aniline. Both in the solid state and when dissolved in benzene it is remarkable for its greenish fluorescence and banded, fluorescent spectrum, and broad and well-defined absorption bands. In the benzene solution, 2 are seen between F and G, and another slightly more refrangible than G. When the substance is examined in the solid state, the bands are nearer the red end of the spectrum.

Acridine, $C_{13}H_9N =$. Acridine is a basic

body which may be isolated by agitating crude anthracene with dilute sulphuric acid, precipitating the solution with potassium chromate, purifying the acridine chromate by recrystallisation, precipitating the base by ammonia, and recrystallising it from hot water. The hydrochloride, which forms golden or brownish-yellow scales, may also be employed for the purification of the base. Acridine forms

colourless or brownish-yellow, rhombic prisms. It melts at 110°, sublimes in broad needles at about 100°, boils unchanged at 360°, and distils with the vapour of water. It is slightly soluble in cold, but more readily in boiling water, and is readily dissolved by alcohol, ether, carbon disulphide, benzene, etc. Acridine exhibits a feeble alkaline reaction, and combines with acids to form a series of yellow salts, all of which are crystallisable and most of them easily soluble. They suffer decomposition when boiled with a large quantity of water. In dilute solution acridine salts exhibit a strong blue fluorescence, which is green with more concentrated solutions, and disappears if they are very strong. With strong nitric acid acridine forms nitro-compounds. Sulphuric acid has no action except at a very high temperature, and potassium hydroxide does not react below 280°. By oxidising agents acridine is unaffected. Its most characteristic property is an irritating effect on the skin and mucous membrane. Violent sneezing and coughing are produced on inhaling the smallest particle of the dust or vapour, and even very dilute solutions of its salts cause acute stinging when applied to the skin or tongue. It has been used as an insecticide, and compositions containing it have been used for coating the bottoms of vessels. The preservative properties of coal-tar creosote oil may be in part due to acridine.

Acridine picrate, $C_{13}H_9N,C_6H_3(NO_2)_3O$, is a canary-yellow crystalline salt, which is also wholly insoluble in cold, and is partially decomposed by boiling-water. It melts at 208°, and is but slightly dissolved by alcohol or benzene, even when boiling.

For a more extended account of acridine salts see Vol. 6.

Detection and Separation of Anthracene and Its Associates.

The reactions of anthracene itself have already been detailed. The recognition and separation of the various constituents of crude commercial anthracene are attended with great difficulties. Fractional fusion and distillation are processes suggested by the tables on pages 266, 267, and the employment of suitable solvents and fractional crystallisation therefrom are methods often referred to in the foregoing description of the constituents of crude anthracene. Other useful processes and tests are based on the properties of their compounds with picric acid, on their reactions with concentrated sulphuric acid and with the fused chlorides of bismuth and antimony, and on the nature of oxidation products yielded on treating the solutions in glacial acetic acid with chromic acid.

Behaviour of Solid Hydrocarbons with Solvents.—The follow-ing table, due to G. von Bechi, shows the behaviour of anthracene and it associates with solvents.   The sign ∞ signifies that the substance dissolves in all proportions:

	100 parts of toluene dissolve		100 parts of absolute alcohol dissolve	
	At 15°	At 100°	At 15°	At 78°
Naphthalene...............	31.94	∞	5.29	∞
Phenanthrene.............	33.02	∞	2.62	10.08
Anthracene...............	0.92	12.94	0.076	0.83
Pyrene....................	16.54	Very soluble.	1.37	3.08
Chrysene.................	0.24	5.39	0.097	0.17
Anthraquinone............	0.19	2.56	0.05	2.25
Carbazol.................	0.55	5.46	0.92	3.88
Imidophenylnaphthyl.......	Scarcely soluble.	0.39–0.57	Scarcely soluble	0.25

Figures showing the behaviour of anthracene itself with some solvents are given on page 262.   The comparatively slight solubility of anthra-cene in alcohol, carbon disulphide, and petroleum spirit was formerly applied to the assay of the commercial substance.

The following data are due to W. H. Perkin:

	100 parts of petroleum spirit boiling between 70° and 100° dissolve	100 parts of coal-tar naphtha boiling between 80° and 100° dissolve
Phenanthrene...........	3.207	21.94
Anthracene.............	0.115	0.976
Dichloranthracene.......	0.137	0.52
Anthraquinone..........	0.013	0.166
Carbazol...............	0.016	0.51

A process has been given by Zeidler[1] for the further separation by solvents of such of the constituents of crude anthracene as are dis-solved by acetic ether.

Compounds of Solid Hydrocarbons with Picric Acid.

Most of the constituents of crude anthracene form characteristic crystalline compounds with picric acid, which have the general formula

[1] *J. Soc. Chem. Ind.*, 1892, 98.

$MC_6H_3(NO_2)_3O$, in which M represents a molecule of the hydrocarbon. In some instances this reaction affords a valuable means of recognising the hydrocarbon. These so-called "picrates" are usually decomposed by water or alkaline solutions, and in some cases even by alcohol. To produce them a saturated solution of the hydrocarbon in hot benzene should be mixed with an approximately equivalent quantity of picric acid, also dissolved to saturation in hot benzene, and the mixed solution then allowed to cool. In other cases alcohol may be substituted for the benzene; for the detection of naphthalene, cold alcoholic solutions should be employed. The following is a description of the compounds of picric acid with the more important substances of this class:

Naphthalene is the only solid hydrocarbon, except pyrene and pseudophenanthrene, giving a precipitate when its cold alcoholic solution is mixed with a cold alcoholic solution of picric acid. It forms stellate groups of yellow needles, melting at 149°.

Diphenyl forms no definite crystalline compound.

Acenaphthene.—The compound forms orange-yellow needles on cooling the boiling alcoholic solution.

Fluorene.—The compound crystallises from benzene in slender red needles, melting at 81°.

Phenanthrene.—The compound crystallises from benzene in yellow needles, melting at 145° and soluble in hot alcohol without decomposition.

Pseudophenanthrene.—The compound forms readily on mixing saturated cold alcoholic solutions of hydrocarbon and picric acid. It crystallises in light-red needles, melting at 147°.

Anthracene.—The compound is deposited from solution in hot benzene in ruby-red crystals, very soluble with red colour in a little alcohol, the solution being decolourized and compound decomposed on adding more alcohol.

Fluoranthrene.—The compound forms reddish-yellow needles, melting at 182°, difficultly soluble in cold alcohol, and decomposed by boiling with water.

Pyrene.—The compound is deposited from hot alcohol as a red crystalline precipitate or long dark-red needles, melting at 222°, nearly insoluble in cold alcohol, but very soluble in benzene and decomposed slowly by boiling with water.

Retene.—The compound forms orange-yellow needles, readily soluble in alcohol.

Chrysene.—The compound crystallises from benzene in orange needles. It is decomposed by cold alcohol.

Benzerythrene.—The compound is deposited from very concentrated, hot alcoholic solutions in brownish-yellow flocks.

Carbazol.—The compound forms large red prisms, fusing at 182°.

Acridine forms a true picrate (see page 273).

Quantitative Estimation.

The reaction with picric acid has been made the basis of a method of estimating several of these hydrocarbons and their derivatives (F. W. Küster, *Ber.*, 1894, 1101).

If substances that form insoluble compounds with picric acid be digested on the water-bath with a measured quantity of an aqueous solution of picric acid, nearly saturated at ordinary temperatures— about n/20—the original substance gradually disappears, and in its place an equivalent quantity of the picric acid compound separates quantitatively, either at once or on cooling. The amount of picric acid in the original solution and in an aliquot portion of the filtrate from the molecular compound can be estimated by titration with barium hydroxide (using lacmoid as indicator), and the quantity of picric acid contained in the precipitate calculated.

The digestion on the water-bath must take place in hermetically closed vessels. The substance to be determined, together with the measured volume of picric acid of known strength in excess, is placed in a flask, which must be nearly filled with the solution. The flask is closed with a good india-rubber stopper, through which passes a tube about 7 cm. long. The tube is sealed up at the lower end, and about 1.5 cm. above the sealed end a small hole is blown in the side. When the side hole is just below the stopper, the air in the flask may be pumped out; then, on withdrawing the tube until the sealed end is flush with the under side of the stopper, the flask, having a vacuum in the upper part, may be disconnected from the pump and safely heated in the water-bath. The flask must be heated until the reaction is complete (2 hours—2 days), and frequently shaken during cooling, in order to wash down any material which may have sublimed into the upper part of the flask. After standing for a few hours, the picric acid in the filtrate is estimated by titration. Test analyses show

that the method is exact, except in the case of β-naphthol, with which a correction must be introduced owing to the solubility of the molecular compound. For every 100 c.c. of picric acid solution, 0.0075 grm. of β-naphthol remain unprecipitated.

Reactions of Solid Hydrocarbons with Metallic Chlorides.

Watson Smith has proposed to employ fused antimonous chloride and bismuthous chloride as reagents for the discrimination of solid hydrocarbons. For this purpose a small quantity of the crystallised chloride is placed in a small porcelain crucible and melted, and then further heated over a small flame. A small particle of the hydrocarbon to be tested is next placed on the side of the crucible, which is then so inclined that the melted chloride comes in contact with it. Fusion follows, accompanied in many cases by a colouration. On restoring the crucible to a vertical position, the coloured spot elongates and forms a coloured streak. Tested in this way, the hydrocarbons give the reactions shown in the following table:

Hydrocarbon	Reaction with antimonous chloride	Reaction with bismuthous chloride
Naphthalene, pure.......	No colouration. During cooling, characteristic rhombic tables form in the fused chloride.	No colouration. During cooling, yellow, transparent needles separate.
Naphthalene, impure.....	More or less carmine colouration.	More or less orange colouration.
Diphenyl...............	No colouration	No reaction.
Phenanthrene..........	Difficultly soluble. Faint greenish colouration.	Brown or greenish-brown.
Anthracene............	Traces even give a yellowish-green colour. Colourless needles formed during cooling.	Purple-black colouration; very characteristic.
Dinaphthyls............	No colouration..........	No reaction.
Pyrene................	Same as phenanthrene ...	....
Chrysene..............	Traces even produce golden-yellow colour.	....
Stilbene...............	At 40° smallest trace gives orange colour, destroyed at higher temperature.	....
β-Phenylnaphthalene.....	No reaction............	....
Triphenylmethane.......	No reaction. Greenish colour with excess.	....

Behaviour of Solid Hydrocarbons with Chromic Acid.

When treated with oxidising agents, anthracene and many of the bodies occurring in association with it yield characteristic oxidation products. The best method of obtaining these bodies is to act on the hydrocarbons by a solution of chromic acid in glacial acetic acid. When the object is to obtain the immediate products of the oxidation, the treatment should be of limited duration and the oxidising agent should be employed in theoretical quantity or very moderate excess, but otherwise the process should be conducted as described on page 282. The following is an epitomised account of the products obtained by the action of chromic acid in acetic solution on the principal constituents of crude anthracene:

Naphthalene is apt to be completely oxidised to carbon dioxide and water, but by careful treatment may be converted into naphthaquinone, $C_{10}H_6O_2$, and ultimately into phthalic acid, $C_8H_6O_2$.

Acenaphthene is oxidised to naphthalic acid, $C_{12}H_8O_4$.

Diphenyl yields benzoic acid, $C_7H_6O_2$.

Fluorene is oxidised to fluorenone diphenylene-ketone, $C_{13}H_8O$, which is volatile in a current of steam, and is deposited in crystals from its solution in alcohol.

Phenanthrene is transformed by the chromic acid mixture into phenanthraquinone, $C_{14}H_8O_2$, and this is ultimately converted into diphenic acid, which is susceptible of still further oxidation. Phenanthraquinone crystallises in dark orange-yellow prisms, melting at 198°. It is sparingly soluble in hot water, but dissolves freely in benzene and acetic acid. Ignited with soda-lime it yields diphenyl, $(C_6H_5)_2$ in almost the theoretical proportion, whereas anthraquinone gives benzene when similarly treated. The 2 bodies also differ in their behaviour with the acid sulphites of the alkali metals, with which anthraquinone does not combine. Phenanthraquinone, when warmed with solution of sodium hydrogen sulphite, is dissolved and may be reprecipitated by mixing the filtered liquid with hydrochloric acid. This reaction may be used for the detection of phenanthrene. The hydrocarbon is oxidised by warm chromic acid mixture, the oxidation-product treated with alkali, and then warmed with the sulphite solution. Pyrenequinone gives a similar reaction.

If a few drops of *commercial* toluene be added to a dilute solution of phenanthraquinone in glacial acetic acid, and, after thoroughly

cooling, concentrated sulphuric acid be then added, drop by drop, and the resultant solution treated with water after a few minutes, a colouring matter separates out which is dissolved with splendid violet-blue colouration on agitation with ether. This reaction depends on the presence of methylthiophene (thiotolene), C_5H_6S, in the toluene used (see page 211).

Pseudophenanthrene yields a yellow quinone, fusing at 170° and soluble with facility in alcohol and cold benzene.

Anthracene is converted by the chromic acid treatment into anthraquinone, $C_{14}H_8O_2$, which is an exceedingly stable body, resisting further action to a remarkable degree. Its properties have already been fully described.

Methylanthracene is converted into soluble anthraquinone-carboxylic acid, $C_{14}H_7O_2 . COOH$.

Fluoranthrene is converted by the chromic acid mixture into fluoranthraquinone, $C_{15}H_8O_2$, and an acid soluble in alkaline liquids.

Pyrene yields pyrenequinone, $C_{16}H_8O_2$, which forms reddish crystals. It yields finally, and with some difficulty, products soluble in alkali.

Retene forms retenequinone, $C_{18}H_{16}O_2$, and other products. Retenequinone is a brick-red powder, crystallising from alcohol in orange-red needles, melting at 197°. It can be further oxidised only with great difficulty, and is insoluble in cold and dilute soda, but is dissolved by hot concentrated alkalies.

Chrysene yields chrysoquinone, $C_{18}H_{10}O_2$, and is afterward converted, with some difficulty, into phthalic acid, $C_8H_6O_2$. Chrysoquinone has a deep-red colour, melts at 235°, and dissolves in strong sulphuric acid with deep indigo-blue colouration.

Benzerythrene yields soluble products under the chromic acid treatment.

Chrysogene, said to exist in considerable quantity in certain kinds of anthracene (see page 270), is alleged to be completely and readily converted into soluble products by the chromic acid mixture. This is doubtful, for—

Imidophenylnaphthyl (described on page 272), yields a quinone of the formula $C_{16}H_9N_2O_2$, which forms reddish-yellow needles and obstinately resists further oxidation. It appears always to be produced by the oxidation of anthracenes which give banded absorption-spectra, and leads to excessive estimates of the yield of real anthra-

cene. The quinone is destroyed by prolonged treatment with fuming sulphuric acid at 100°.

Behaviour of Solid Hydrocarbons With Benzal Chloride.

E. Lippmann and J. Pollak (*Monatsh.*, 1902, **23** (6), 670–671) have devised the following tests:

The colour reactions given in the following table are observed by suspending the hydrocarbons in concentrated sulphuric acid and adding in the cold a few drops of benzal chloride (benzylidene chloride), $C_6H_5CHCL_2$.

Hydrocarbons	Colour
Anthracene	Malachite green.
Naphthalene	Magenta.
*Benzene	Light yellow. ⎫ Colours varying with the
*Toluene	Light yellow. ⎬ degree of purity.
*Xylene	Orange. ⎭
Phenanthrene	Carmine.
Triphenylmethane	Faint yellow.
Picene	Olive-green after a short time
Diphenylmethane	Brick-red.
Stilbene	Bluish-green.
*Pseudocumene	Orange-red.
*Chrysene	Orange.
Pyrene	Emerald-green becoming deep blue.
Acenaphthene	Dark blue.
Dibenzylanthracene	Yellowish-green.
Chrysene	Light yellow, then light green, and finally dark olive-green.

The paraffin in crude anthracene is practically unaltered by treatment with the chromic acid mixture.

A dark green hydrocarbon, fusing at 271°, is occasionally present in anthracene. It is soluble with difficulty in glacial acetic acid, and should, if present, be separated as far as possible by this solvent before employing the chromic acid mixture, as its oxidation is very difficult to effect.

Assay of Crude Anthracene.—Commercial crude anthracene is a green or brownish-green friable mass or crystalline powder. It contains a very variable percentage of real anthracene, the usual propor-

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* The hydrocarbons marked with an asterisk give the same colour with sulphuric acid alone, no alteration taking place on the addition of benzol chloride.

tion being from 30 to 40%, though formerly 15% was common, and special makes now assay over 80%. It cannot be too strongly insisted on that the true value of a sample of crude anthracene is dependent not merely on the proportion of real anthracene contained in it, but also on its comparative freedom from objectionable impurities.

The *paraffin* existing in Scotch and north-country anthracenes has a high m. p., and little solubility in either petroleum or coal-tar naphtha. It dissolves in the hot liquids, but is almost entirely deposited on cooling. A small percentage of this paraffin greatly impedes the subsequent treatment of the anthracene, and, being a very stable substance, it passes through most of the processes unchanged. Experience has proved that in the operation of oxidising anthracene on a large scale, by treatment with potassium bichromate and dilute sulphuric acid, all other admixtures may be dealt with and to a great extent removed, but paraffin resists the oxidising action, melts, and retards the operation to a hopeless extent. Hence a search for this objectionable impurity should never be omitted, unless it be known to a certainty that bituminous shale or cannel coal has had no share in the production of the sample. It may be detected and estimated in crude anthracene in the following manner: 10 grm. of the sample is treated with 108 c.c. of strong sulphuric acid. The mixture is heated on a water-bath for about 10 minutes, or until the anthracene is completely dissolved. Any considerable quantity of paraffin will rise to the surface in the form of oily globules. The solution obtained is cautiously poured into 500 c.c. of water contained in a tall beaker. After being thoroughly stirred the liquid is allowed to cool, when any paraffin will rise to the surface, and, having solidified, can be removed, washed with a little cold water, dried between blotting paper, and weighed. From 2 to 5% is the quantity commonly present in Scotch anthracenes.

Hensler and Herde (*Zeit. f. ang. Chem.*, 1895, 283) employ the following method for estimating the paraffin in crude anthracene: 2 grm. of the sample are weighed into a 150 c.c. flask, and fuming nitric acid added slowly—at first, drop by drop—the flask being kept cooled by ice-water. After the mass has been completely digested with the acid the flask is warmed on the water-bath until the undissolved material melts. The mixture is allowed to cool, filtered through asbestos, the filter washed thoroughly with fuming nitric acid, and then with water until a drop of the filtrate gives no turbidity

with water. The filter is washed with alcohol and subsequently by warm ether to dissolve the paraffin. The alcohol filtrate is evaporated in a weighed dish, the ether solution added and evaporated, the residue dried for 30 minutes at 105° to 110° and weighed.

According to B. Nickels, samples of crude anthracene containing *phenylnapthylimide* show the highly characteristic absorption spectrum of this substance; 2 broad, well-defined black bands between F and G and another slightly more refrangible than G. Samples exhibiting these bands are purified with some difficulty, and yield by oxidation an impure anthraquinone containing many amorphous particles. For observing the spectrum of the sample, about 1.25 grm. should be be dissolved in 6 c.c. of warm benzene, the liquid passed through a dry filter, and observed with a spectroscope. A micro-spectroscope or a direct-vision pocket spectroscope will suffice. The intensity of the absorption-bands is an approximate measure of the objectionable impurities of the sample.

Carbazole and phenanthrene in anthracene are detected, according to H. Behrens (*Chem. Centr.*, **2**, 540 (1902), as follows: The sample is extracted in the cold with acetic ester, the solution allowed to evaporate and the residue transferred by the aid of a few drops of the same solvent to a watch glass. On evaporation the carbazole is left behind; when treated with a drop of nitro-benzene and phenanthraquinone, it yields characteristic small copper-coloured plates. Phenanthrene is detected by extracting with benzene and treating the evaporation residue of the extract with a di-nitrophenanthraquinone dissolved in nitro-benzene.

Anthraquinone Test.—For the *quantitative* assay of commercial anthracene the most satisfactory method is that based on the formation of anthraquinone by the action of chromic acid. This is a characteristic, insoluble substance, not liable to further change, while nearly all the associates of anthracene are, by the same treatment, either completely oxidised or else converted into products readily removed by water or dilute alkali.

This method was first proposed by E. Lück, and, with suitable modifications, affords a very satisfactory solution of a difficult problem. The following mode of operating is essentially that of Meister, Lucius, and Brüning, with some precautions and modifications recommended by G. E. and T. H. Davis, who verified the accuracy of the method by operating on pure anthracene and impure samples of known compo-

sition. The test is commercially known as "Meister, Lucius, and Brüning's anthraquinone test, with appendix." 1 grm. of the carefully sampled specimen is placed in a flask of 500 c.c. capacity. 45 c.c. of the very strongest glacial acetic acid is then added, and an inverted condenser or long glass tube adapted to the flask. The liquid is then brought to the b. p., and, while boiling, the chromic acid is added to it gradually, drop by drop, by means of a tapped funnel passing through the india-rubber stopper of the flask, or inserted in the top of the vertical condenser (Fig. 9). The chromic acid solution is prepared by dissolving 15 grm. of crystallised chromic anhydride (perfectly free from lead salts and insoluble matter generally) in 10 c.c. of water and 10 c.c. of glacial acetic acid. The addition of the oxidising agent should occupy 2 hours, and the contents of the flask should be kept in continued ebullition for 2 hours longer, 4 hours in all being necessary to ensure complete oxidation of the impurities. The flask is then left at rest for 12 hours, when the contents should be diluted with 400 c.c. of cold water and allowed to rest another 2 hours. The precipitated anthraquinone is then filtered off and well washed with cold water. It is next washed on the filter with a boiling-hot 1% solution of sodium hydroxide, and again thoroughly washed with boiling water, about 300 c.c. being employed. The anthraquinone, which should exhibit no alkaline reaction, is then rinsed from the filter into a small dish by means of a jet of water, the water evaporated off, and the residue dried at 100° and weighed.

The anthraquinone obtained in the foregoing manner is rarely sufficiently pure to allow of the percentage of real anthracene in the sample being at once calculated from its weight. Several methods have been proposed for the further purification of the crude product, but the following improved "appendix" by Meister, Lucius, and Brüning, commercially known as the "sulphuric acid test of October, 1876," is now universally employed. The crude anthraquinone is mixed in the dish in which it was weighed, with 10 times its weight of fuming sulphuric acid having a sp. gr. of 1.880 at 60° F., and the whole heated to 100° on a water-bath for 10 minutes. The solution obtained is next left in a damp place for 12 hours to absorb water. 200 c.c. of cold water are then added, the precipitated anthraquinone collected on a filter, and washed free from acid with cold water, then with about 100 c.c. of boiling sodium hydroxide solution (1%), and finally with about 400 c.c. of boiling water. The character of the

quinone is an indication of its purity, a deep yellow or orange tint indicating the presence of phenanthrene- or chrysene-quinone. The latter body is also recognised by the production of an indigo-blue colouration on adding the sulphuric acid. With impure anthraquinones both the acid filtrate and the alkaline washings are deeply coloured—brown, purplish, and bluish tints being the most common.

The greater part of the moist anthraquinone is then transferred to a flat platinum or porcelain dish by means of a spatula, the remaining portion being rinsed off the filter into the dish by means of a fine jet of water. The water is then evaporated off at 100°, and the residue weighed. An alternative method is to dry the anthraquinone on the filter, and then remove it. To avoid loss, the stained portion of the filter may be cut small and heated in a test-tube with about 1 c.c. of benzene. The resultant solution is poured off into a small dish, and the residue obtained by its evaporation added to the main quantity of anthraquinone. The difference in the result caused by the benzene treatment often amounts to 0.2% of the crude anthracene, owing to the loss in the other methods by imperfect removal from the filter. Hence, when the analyst is not limited by the conditions of the contract note, treatment of the filter with benzene should not be neglected. Either of the foregoing methods of treatment is preferable to weighing the anthraquinone on the filter, which is apt to be altered in weight by the reagents employed, though this source of error may be to a great extent avoided by using a double filter, the apex of the outer one being cut off. The weights of the 2 filters are accurately adjusted before use by trimming with a pair of scissors, and on weighing the anthraquinone, the outer filter is used as a counterpoise to the inner.

H. Bassett (*Chem. News*, **73** (1896), 178) has proposed the following modification of this method: After the washing of the anthraquinone collected on the filter, it is dried in the water-oven and then transferred to a flask of the usual size, with a short and wide neck, using a small wash-bottle containing 45 c.c. of glacial acetic acid to rinse the filter-paper and funnel. (The hardened filter-paper now furnished would probably serve well.) 10 c.c. of pure nitric acid (sp. gr., 1.4) and 2.5 c.c. of chromic acid solution are added, and the mixture boiled for an hour, using a reflux condenser. The flask is allowed to stand overnight, then diluted to 400 c.c., filtered, washed with water, and then with boiling solution of sodium hydroxide as above Bassett (*Chem. News*, **71** (1895), 202) states that samples of

chromic anhydride often contain considerable sulphuric acid, but this does not interfere seriously with the test.

The weight of anthraquinone thus obtained ought not to be regarded as representing that of the pure product, as it usually contains extraneous matters, such as *sand*, and frequently *chromium*. Some anthracenes yield anthraquinones which carry much chromium sesquioxide. Hence the dish should be gradually heated so as to completely sublime the anthraquinone, and the residue obtained deducted from the weight previously found. This corrected weight of the anthraquinone, multiplied by the factor 0.856, gives the real anthracene in the weight of the sample employed.

The *anthraquinone* obtained by the above process should be crystallised and of a uniform pale-yellow colour. The purer it is, the paler the colour. Certain strange quinones are apt to be present in some cases, and are recognisable by the modified form of the crystals and the colour of the product. Phenanthraquinone is orange, and chrysene-quinone deep red. Continued treatment with the chromic acid mixture removes all these bodies, but does not affect the quinone, $C_{16}H_9NO_2$, produced by the oxidation of imido-phenylnaphthyl referred to on page 272 as giving a characteristic absorption-spectrum. This substance, unlike the quinones from phenanthrene, chrysene, etc., tends to prevent the crystallisation of the anthraquinone, and is one of the sources of the so-called "amorphous particles" which are frequently present in sufficient quantity to obliterate all trace of crystallisation in the oxidised product. This troublesome impurity may, however, be destroyed by a somewhat longer-continued heating with sulphuric acid in the manner already described, and hence this supplementary treatment should never be omitted in the case of samples which originally showed absorption-bands, or which have produced crude anthraquinones of unhealthy appearance.

Estimation of Anthracene in Tar and Pitch.—For the estimation of anthracene in coal-tar, C. Nicol (*Ztschr. anal. Chem.*, 1875, 318) distils 20 grm. in a small luted retort, and the vapours are received in a U-tube, kept at 200° by being immersed in a bath of hot paraffin. The more volatile products are not condensed, but the anthracene and other hydrocarbons of high b. p. collect in the U-tube. Care must be taken to prevent bumping and the condensation of the distillate on the neck and sides of the retort. When the contents of the retort become coked, the process is stopped and the neck is cut off, pounded,

and the powder added to the distillate.   The whole is then dissolved in glacial acetic acid, and subjected to oxidation with the chromic acid mixture in the manner already described.   Watson Smith considers 20 grm. far too small a quantity.   He operates on at least a litre, and rejects the portion distilling just before coking, as it contains much resinous matter of an objectionable kind, and would not in practice be treated for anthracene.   The anthracene oil is well mixed and an aliquot part oxidised.

In some cases it is preferable to reject the fraction distilling between 200° and 250° as it contains little or no anthracene, and in tars rich in naphthalene is so large in quantity as materially to impede the subsequent treatment.   The anthracene may be further concentrated by cooling the heavy oils to a low temperature, filtering, and pressing the deposit of solid hydrocarbons between folds of filter-paper.   The crude anthracene thus obtained is then oxidised to anthraquinone in the usual way.   Ordinary gas-works coal-tar contains from 0.3 to 0.5% of real anthracene, but from the tar obtained from Simon-Carvès coke-ovens Watson Smith obtained 0.73% of anthracene, and A. H. Elliott found as much as 2.63% in the tar produced in the manufacture of water-gas from petroleum naphtha.

PHENOLS.

By S. S. SADTLER.

The bodies termed phenols are intermediate in character between acids and the true aromatic alcohols, of which benzyl alcohol is the type.

The monohydric phenols have the general formula $C_nH_{2n-7}OH$. Of these, phenol and cresol are described in the following sections. Thymol, $C_{10}H_{13}OH$, which is a higher homologue of these bodies, will be considered in connection with the essential oils. The naphthols, $C_{10}H_7OH$, which are closely related to the monatomic phenols, are described on page 252.

The Dihydric Phenols or Hydroxyphenols, $C_nH_{2n-8}\cdot(OH)_2$, are described on page 335. Catechol (or pyrocatechin), resorcinol, and quinol (or hydroquinone) are isomeric substances of the formula $C_6H_4(OH)_2$. Orcinol, or orcin, $C_7H_6(OH)_2$, obtained from various lichens, is a phenol homologous with resorcinol.

The trihydric phenols or dihydroxyphenols are represented by pyrogallol and phloroglucinol, $C_6H_3(OH)_3$.

Certain ethers of catechol and pyrogallol are described in the section on "Wood-tar Creosote" (page 347), in which liquid they are present in large proportion.

MONOHYDRIC PHENOLS. $C_nH_{2n-7}OH$.

The monohydric phenols form a homologous series, of which phenol proper, or carbolic acid, is the first member, and the cresols form the next homologue.

Of the higher members of the series, some exist in the tars produced by the distillation of coal and wood (*e. g.*, xylenols); others in certain natural essential oils (*e. g.*, thymol); while others again have hitherto been obtained by synthetical reactions only. The higher monohydric phenols present a close resemblance to phenol in their general characteristics. They may be distilled without decomposition, are but

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slightly soluble in water, but dissolve readily in aqueous alkalies, alcohol, and ether.

The monohydric phenols may be regarded as being formed from benzene and its homologues by the substitution of a molecule of hydroxyl for an atom of hydrogen in the principal chain. All but the lowest term are susceptible of isomeric modifications, according to the relative positions of the hydroxyl and other substituted radicals in the benzene nucleus.

The difference in structure between the monohydric phenols and the true aromatic alcohols, typified by benzyl alcohol, is shown by the following example, all four bodies having the empirical formula C_7H_8O:
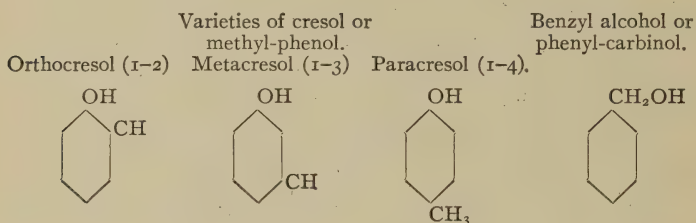
The monohydric phenols are distinguished from the *alcohols of the benzyl series* by the following reactions:

a. Hydrochloric acid is without action on the phenols, but (*e. g.*) converts benzyl alcohol into benzyl chloride, $C_6H_5CH_2Cl$.

b. Phenol readily dissolves in concentrated sulphuric acid to form phenolsulphonic acids, while benzyl alcohol is resinified by similar treatment.

c. On treatment with oxidising agents the phenols yield quinones, but benzyl alcohol yields benzoic acid.

d. Nitric acid converts the phenols into well-characterised nitro-derivatives of acid character, but benzyl alcohol is oxidised by the same reagent to benzoic aldehyde and benzoic acid.

e. The phenols dissolve in solutions of alkalies to form compounds in which they play the part of an acid. The acid character is less marked in the higher members of the series, but the chloro- and nitro-derivatives have strongly acid properties, not only dissolving in solutions of alkaline hydroxides, but decomposing carbonates with effervescence and forming definite and stable salts.

f. Ferric chloride produces a characteristic blue or violet colour with many of the phenols and their derivatives.

g. On adding hydrochloric acid to the aqueous solution of a phenol, immersing a slip of pine-wood and allowing it to dry, a blue colour is developed.

h. The phenols react immediately with excess of bromine water to form bromo-derivatives (usually containing Br_3), which are usually white or yellowish, and are insoluble or nearly insoluble bodies.

The reactions of the phenols of serivce for their recognition are described more in detail on page 295.

PHENOL. CARBOLIC ACID.

Hydroxybenzene. C_6H_5OH.

Phenol is formed in various analytical and synthetical reactions, but the principal source of commercial interest is the fraction of coal-tar distilling between 150° and 200°. On treating this with sodium hydroxide, phenol and its homologues are dissolved, together with a certain amount of naphthalene and other indifferent bodies. These are partially precipitated on diluting the alkaline liquid, and become further oxidised on exposing the solution to the air. On treating the liquid with an excess of sulphuric acid the liberated phenols form an oily layer, which is separated, from the aqueous liquid. From the crude material so obtained, pure phenol is obtained by fractional neutralisation, the homologues having less defined acid properties. On again liberating the phenol from its sodium compound a product is obtained which is fractionally distilled. The portion passing over within a few degrees of 182° is subjected to a freezing mixture, when crystals of phenol form, which are separated from the liquid by a centrifugal machine. The product may be further purified by a repetition of the process.

For the synthetic preparation of phenol several methods may be employed, 2 of which are of sufficient importance to be briefly described (H. W. Jayne, *Amer. Jour. Pharm.*, 1891): The first, or sulphonate method, is similar to that used in preparing the naphthols. Pure benzene, free from thiophen, is placed with about 5 times its weight of strongest commercial sulphuric acid in closed cast-iron pots. While the mixture is slowly stirred the vessel is gently heated with steam in such a manner that the vapours of benzene which pass over into

the cooler are continually returned to the kettle. After a number of hours the reaction is finished, and the benzene not acted on is collected as it flows from the cooler. The crude benzenesulphonic acid formed, mixed with the excess of sulphuric acid, is allowed to cool, and then diluted with water in a lead-lined tank. Slaked lime is added to the hot solution in sufficient quantity to render it faintly alkaline, and the calcium sulphate formed separated by means of a filter-press. The clear liquor containing calcium benzenesulphonate is treated with sufficient sodium carbonate to precipitate all the calcium as carbonate, and the filtered liquid is evaporated to dryness, leaving the sulphonate as a white powder. Sodium hydroxide is then melted in a cast-iron kettle, and small portions of the dry sodium benzenesulphonate, prepared as above, are gradually added, the whole being kept in quiet fusion for some time. The melt now contains sodium phenate, sodium sulphite, and the excess of sodium hydroxide:

$$C_6H_5SO_3Na + 2NaOH = C_6H_5ONa + Na_2SO_3 + H_2O.$$

It is ladled from the kettle into pans and allowed to cool, broken up, dissolved in water, and the solution acidified with sulphuric or hydrochloric acid. The phenol thus liberated separates from the concentrated salt solution, and is distilled.

In melting the sodium benzene-sulphonate with sodium hydroxide it is necessary, in order to obtain a good yield, to use a very large excess of the latter. A better yield is obtained with potassium hydroxide.

It has been proposed to treat the melt, after dissolving in water, with carbon dioxide, which would liberate the phenol equally as well as a stronger acid, and in addition would form sodium or potassium carbonate, which, together with the sulphite already present, could be converted into the hydroxide by treating with lime, and this used for a second operation.

The second method is much simpler. A pure aniline oil, preferably that grade called "aniline for blue," is dissolved in water in a lead-lined tank covered with a hood, and provided with stirrers and leaden steam-coils. The solution is acidified very strongly with sulphuric acid, and to the hot liquid a solution of commercial sodium nitrite is gradually added, when phenol is at once formed.

In this reaction the sodium nitrite in contact with the acid solution liberates nitrous acid, which forms diazobenzene sulphate with the aniline sulphate:

$$(C_6H_5NH_2)_2H_2SO_4 + 2HNO_2 = (C_6H_5N_2)_2SO_4 + 4H_2O;$$

but, as the solution is hot, the diazo-compound at once decomposes, with the formation of phenol and evolution of nitrogen:

$$(C_6H_5N_2)_2SO_4 + 2H_2O = 2C_6H_5OH + H_2SO_4 + 4N.$$
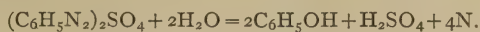
Pure phenol may be prepared by heating crystallised salicylic acid, either alone or mixed with pounded glass or lime, strongly and rapidly in a glass retort. Phenol passes over into the receiver, and crystallises almost to the last drop.

Pure phenol is a colourless solid, crystallising in long needle and melting at 42.2° to a colourless, limpid fluid, slightly heavier than water, which boils at 18° and distils without decomposition. Specimens having a lower m. p. than 42° contain cresols or water. The taste of phenol is biting, but at the same time sweet. The odour is usually strong and characteristic, but both smell and taste are much less marked in pure specimens than in the crude article.

The United States Pharmacopœia contains the following specifications and tests for a phenol of medicinal purity, but not absolutely pure phenol.

Colourless, interlaced, or separate needle-shaped crystals, or a white, crystalline mass, sometimes acquiring a reddish tint; having a characteristic, somewhat aromatic odour; when copiously diluted with water, it has a sweetish taste, with a slightly burning after-taste, and, when undiluted, cauterizes and whitens the skin and mucous membrane.

Soluble in 19.6 parts of water at 25° (77° F.), the solubility varying according to the degree of hydration of the phenol; very soluble in alcohol, ether, chloroform, benzene, carbon disulphide, glycerin, fixed and volatile oils; almost insoluble in petroleum benzin.

When gently heated, phenol melts, forming a highly refractive liquid. It is also liquefied by the addition of about 8% of water. If the phenol be liquefied by a gentle heat, and then slowly cooled under constant stirring, until it is partly recrystallised, the semi-liquid mass should have a temperature (remaining stationary for a short time) not lower than 40° (104° F.).

Phenol should have a b. p. not higher than 188° (370.4° F.). A lower b. p. or a higher m. p. indicates a less hydrated phenol. When heated upon a water-bath, it should be volatilised without leaving a residue. The vapour is inflammable.

Phenol is faintly acid to blue litmus paper.

Its aqueous solution yields, with bromine water, a white precipitate

of tribromphenol, which at first redissolves, but becomes permanent as more of the reagent is added, and appears crystalline when viewed under the microscope.

On adding to 10 c.c. of an aqueous solution of phenol (1 in 100) 1 drop of ferric chloride T. S., the liquid acquires a violet-blue colour, which is permanent.

1 volume of cold, liquefied phenol (rendered liquid by the addition of 8% of water) forms, with 1 volume of glycerin, a clear liquid which is not rendered turbid by the addition of 3 volumes of water (absence of creosote and of cresol). The crystals of phenol readily absorb water from the air, whereby the fusing-point is lowered.

MELTING-POINTS OF AQUEOUS PHENOL.[1]

Temperature, °	Of phenol, %	Of water, %
42.1	100	0.00
42	99.97	0.03
41	99.67	0.33
40	99.37	0.63
39	99.07	0.93
38	98.77	1.23
37	98.47	1.53
36	98.17	1.83
35	97.87	2.13
30	96.32	3.68
25	94.65	5.35
20	92.77	7.23
15	90.51	9.49
10	87.70	12.30

In hot water phenol is much more soluble, and is miscible in all proportions of about 70°; but in water saturated with sodium chloride or sulphate it is but slightly soluble. *Anhydrous* phenol is miscible in all proportions with alcohol, glacial acetic acid, glycerol, ether, benzene, carbon disulphide, and chloroform. When *aqueous* phenol is shaken with excess of any one of the last 4 solvents, the phenol dissolves and the contained water is separated. According to Staveley, absolute phenol is soluble in petroleum spirit, but is separated by water. This separation is prevented by the presence of from 20 to 25% of benzene.

The above statements as to the solubility of phenol are the result of Allen's personal experience. The solubility is often misstated,

[1] Private communication from Launcelot W. Andrews, St. Louis, Mo.

partly owing to the use of an acid containing cresol, and partly from a confusion between the absolute and the hydrated acid.

Phenol coagulates albumin, is a powerful antiseptic, acts as a caustic on the skin, and is powerfully *poisonous*. Its local action is much influenced by the solvent; it is stated that the solution in pure glycerol or absolute alcohol is scarcely caustic. Strong phenol dissolves gelatin completely, but coagulates it when added to its aqueous solution. Indigo-blue (indigotin) is soluble in hot phenol and may be obtained in crystals on cooling the liquid.

By the action of fused sodium hydroxide on phenol, phloroglucinol, catechol, and resorcinol are formed, together with other products.

Phenol is converted by the action of chlorine and bromine into chloro- and bromo-derivatives (page 298). Nitric acid acts on it with formation of nitrophenols. Concentrated sulphuric acid converts phenol into phenolsulphonic acids. Hydrogen dioxide converts phenol into catechol, hydroquinone, and quinone.

Moist phenol turns red; the colour has been ascribed to various impurities—*e. g.*, thiophen. Kohn and Fryer (*J. Soc. Chem. Ind.*, 1893, 107) have carefully investigated the subject and state that the change is due to the oxidation of the phenol itself, dependent, in part at least, on the absorption of water. A well-known German house advertises a pure phenol, "guaranteed not to redden under the usual precautions of keeping," but the precautions are not stated.

According to J. Walter (*Chem. Zeit. Rep.*, 1899, 47), ferrous salts increase the liability of phenol to turn red, the iron in ordinary bottles being sufficient to cause contamination. Walter states that a sample of phenol that began to redden in 10 days in a bottle made of glass containing iron remained colourless for several months in a bottle of the same kind of glass that had been coated on the inside with paraffin.

PHENOXIDES.

Although its aqueous solution does not redden litmus, phenol is much more soluble in weak alkaline solutions than in pure water. With equivalent amounts of the strong bases it forms compounds which are difficult to obtain in a definite form. The potassium and sodium compounds are readily soluble in water, and the solutions are not decomposed on dilution. *Potassium phenoxide*, C_6H_5OK, obtained by heating phenol with potassium or potassium hydroxide, crystallises

In slender white needles soluble in ether. De Forcrand (Abst.
J. Soc. Chem. Ind., 1893, 618) proposes to distinguish 2 series of de-
rivatives, namely, "true phenates," corresponding to the general
formula C_6H_5HO,MHO, and phenoxides, C_6H_5MO, the substances of
the latter class being capable of assimilating water so as to become
metameric with the phenates.

PHENOL ETHERS.

On heating potassium phenate with alkyl iodides, ethers are
produced. *Methyl phenate*, or anisole, $C_6H_5OCH_3$, is a mobile liquid
of pleasant, aromatic odour, having a density of 0.991 and distilling
unchanged at 152°. It dissolves in strong sulphuric acid to form
anisolsulphonic acid, and with bromine yields substitution prod-
ucts. Ethyoxy benzene phenetole, and amyl phenate resemble the
methylic ether.

PHENOL ESTERS.

Besides the foregoing bodies, which are of the type of the mixed
ethers, many phenol esters are known, but have little practical im-
portance. The production of phenol orthoxalate has been observed to
occur in the manufacture of aurin; phenyl salicylate constitutes the
antiseptic known commercially as "salol."

The solubility of salol in a number of solvents has been determined
by A. Seidell (*J. Amer. Chem. Soc.*, 1907, **29,** 1088–91) as well as the
solubility of several other compounds used as headache remedies.

Solvent	Tempera-ture, °	Solubility % by weight			
		Acet-anilide	Phen-acetin	Caffeine	Salol
Water..................	25°	0.56	0.11	2.14	Insoluble
Ether..................	25°	7.7	1.56	0.27	Insoluble
Chloroform............	25°	16.6	4.76	11.0	Insoluble
Acetone...............	30°–31°	31.15	10.68	2.18	90.99
Benzene...............	30°–31°	2.46	0.65	1.22	88.57
Benzaldehyde..........	30°–31°	18.83	8.44	11.62	?
Amyl acetate..........	30°–31°	10.46	2.42	0.72	85.29
Aniline...............	30°–31°	19.38	9.46	22.89	Very soluble
Amyl alcohol..........	25°	14.00	3.51	0.49	20.44
Acetic acid (99.5%).....	21.5°	32.21	13.65	2.44	63.24
Xylene................	32.5°	1.65	1.25	1.11	87.14
Toluene...............	25°	0.50	0.30	0.57	83.62

Béhal and Choay (*Comp. rend.*, **118**, (1894), 1211) have prepared the *benzoates* of various phenols, and recommend the method for their differentiation. With the exception of the orthocresyl compound, the benzoates are all crystalline solids, insoluble in water, but very soluble in most organic solvents. They are prepared by the action of benzoic chloride on a solution of the phenol dissolved in excess of sodium hydroxide. The table on next page shows the m. p. and b. p. of the phenols and their benzoates, as recorded by Béhal and Choay, whose figures in some cases differ considerably from those of previous observers.

Formula	Compound	Phenol		Benzoate	
		M. p. °	B. p. °	M. p. °	B. p. °
$C_6H_5.OH$	Phenol	42.5–43	178.5	69	298–299
	Orthocresol	30	178.5	liquid	307
C_6H_4MeOH	Metacresol	4	200	54	313–314
	Paracresol	36.5	199	71.5	315.5–316
	Orthoxylenol (1 : 2 : 3)	73	212–213	58	326–327
$C_6H_3Me_2OH$	Orthoxylenol (1 : 2 : 4)	65	222	58.5	333
	Metaxylenol (1 : 3 : 4)	25	208–209	38.5	321
	Para-xylenol	75	208–209	61	318–319
	Ortho-ethylphenol	liquid	202–203	38	314–315
C_6H_4EtOH	Meta-ethylphenol	–4	214	52	322–325
	Para-ethylphenol	45–46	218.5–219	59–60	328

1 : 3 : 5-metaxylyl benzoate melted at 24° and boiled at 326°. 1 : 2 : 3-metaxylenol could not be obtained. Parethylphenol is identical with the substance sometimes called α-ethylphenol.

Qualitative Tests for Phenol.—The following reactions are in most cases common to phenol and the cresols. They do not require that the substance should be in a concentrated state, but are applicable to the aqueous solution. Many of them have been verified by Allen. Various other reactions are described in the sections on "Cresylic Acid" and "Creosote."

a. When a drop of a dilute aqueous solution of phenol is added to a few drops of a solution of 1 grm. of molybdic anhydride in 10 c.c. of concentrated sulphuric acid, contained in a porcelain crucible, a yellowish-brown spot is produced, which rapidly changes to purple, the latter tint being tolerably permanent. Warming the mixture to about 50° greatly assists the reaction, but a higher temperature must be avoided. As this test depends on the deoxidation of the molybdic anhydride, many substances interfere with it.

b. Ferric chloride (avoiding excess) gives a fine violet colour, by which 1 part of phenol in 3,000 of water can be detected. Many allied bodies give a similar reaction (see page 336. The presence of common salt, nitre, or boric acid is unobjectionable, but the reaction is hindered by most mineral and organic acids, acetates, borax, sodium phosphate, glycerol, alcohol, amyl alcohol, and ether.

c. If an aqueous solution of phenol be gently warmed with ammonia and a solution of sodium hypochlorite (avoiding excess), a deep-blue colour is obtained, which is permanent, but turns to red on addition of acids. Solutions containing 1 part of phenol in 5,000 of water react well when 20 c.c. are employed. Much smaller quantities give the reaction after a time.

A modified, and in some respects preferable, method of performing the test is to add to 50 c.c. of the aqueous liquid to be tested 5 c.c. of a mixture of 1 measure of ammonium hydroxide of 0.880 sp. gr. with 9 measures of water, and then drop in fresh and dilute bromine-water very slowly, avoiding excess. The presence of phenol will be indicated by the production of a fine blue tint, which is very permanent. A still better plan is to expose the ammoniacal liquid to the vapour of bromine, avoiding excess of the latter.

d. According to E. Jacquemin, if to a neutral solution of phenol a minute quantity of aniline be first added, and then a solution of sodium hypochlorite be dropped in, the reagent produces yellow striæ, which change to a greenish blue. The reaction is said to be very delicate.

e. If 20 c.c. of a dilute phenol solution be boiled with 5 or 10 drops of Millon's reagent (prepared by dissolving mercury in an equal weight of fuming nitric acid, boiling, and diluting the solution with 2 measures of water), and nitric acid added drop by drop to the hot solution, until the precipitate is redissolved, the mixture assumes a fine blood-red colour, which is permanent for several days. The reaction is exceedingly delicate, but is not peculiar to phenol.

E. Ackermann (*Rev. Chim. Ind.*, 1895, p. 322) obtained the following results when 0.01 grm. of the phenolic substance was acted on by about 20 drops of Millon's reagent: Beechwood creosote gave a reddish-brown colouration in the cold, the colour remaining unaltered after 15 minutes' standing. On heating, the colour changed to brownish-black. Creosol and guaiacol both gave a red colouration in the cold, changing to reddish-brown after 15 minutes. On heating,

the colour became brownish-black. Resorcinol gave an orange colouration in the cold, unchanged after 15 minutes, but changed to deep-red on heating. α-Naphthol gave an immediate red colouration in the cold, and β-naphthol gave a brown colouration on heating. Proteids, some morphine compounds, and various other substances also give with this reagent colourations which are often very similar to those given by phenoloids.

E. Hoffmann modifies this test by pouring 2 or 3 c.c. of the liquid supposed to contain phenol onto the surface of an equal measure of strong sulphuric acid, so as not to cause the liquids to become mixed. A few granules of potassium nitrite are then dropped in, when each particle will produce violet streaks if even a very minute quantity of carbolic acid be present.

Liebermann has observed that strong sulphuric acid to which a 6% solution of potassium nitrite has been added gives a brown colouration, changing to green and blue when gently warmed with phenol or its allies.

f. The phenols give characteristic colour-reactions with chloroform and alkali. The phenol is dissolved in chloroform, a small piece of potassium hydroxide added, and the solution boiled. The characteristic colouration is quickly developed. Reducing and oxidising agents affect the reaction, alcohol sometimes accelerates and sometimes hinders it, ether nearly always impedes it. In aqueous solutions the reaction is less sharp; in this case it is best to shake up with chloroform and proceed with the decanted chloroform as usual, or to extract with ether, boil the ether off, and dissolve the residue in chloroform. When testing for phenols in complex liquids, such as blood or the contents of a stomach, it is best to acidulate and distil in a current of steam. The distillate may then be examined as above.

The results of the test with some members of the phenol group are given below. The following additional data relate to the behaviour of substances not likely to be found in food or beverages when subjected to the foregoing test (Abst. *J. Soc. Chem. Ind.*, 1890, 974):

Metacresol.—As with orthocresol, but a more marked orange shade.

Thymol.—Fine red colouration verging on purple, with a violet tinge, which is accentuated by the addition of a little alcohol or ether, and soon disappears. Limit of sensitiveness, 1 : 20,000.

Guaiacol.—Cherry-red colouration with a blue tinge, changing to violet-blue. Limit of sensitiveness, 1 : 100,000.

Resorcinol.—On warming gently, a cherry-red deposit on the potash and a brownish-yellow colouration of the chloroform; the chloroform ultimately takes up the colour, which is fairly stable. Limit of sensitiveness, 1 : 500,000.

Quinol.—Bluish-green colouration, soon disappearing. Limit of sensitiveness, 1 : 20,000.

Pyrogallol.—A reddish-brown colouration in the cold, which on warming takes on a green tinge, and on boiling soon disappears. Limit of sensitiveness, 1 : 300,000.

Betol.—Bluish-green colouration like β-naphthol. In this last case it is best to boil with a little potassium hydroxide, before adding the chloroform in order to saponify the ester. The colours then obtained are very characteristic.

g. **Reaction of Phenol with Bromine.**—When bromine water is added in moderate excess to an aqueous solution of phenol, a snow-white crystalline precipitate is formed, which readily collects into flocks on agitation, and appears under the microscope in the form of fine stellated needles. In presence of much cresol or of certain other phenols the precipitate loses its crystalline character, and may even assume the form of yellow or reddish oily globules. In extremely dilute solutions the precipitate is only produced slowly; but in 24 hours a solution containing 1/60000 of phenol gives the reaction.

The reaction with bromine is by no means conclusive evidence of the presence of phenol, a similar reaction being produced by homologues of phenol (*e. g.*, cresol, thymol), besides other phenolic substances (*e. g.*, guaiacol, orcinol, pyrogallol, phloroglucol), salicylic acid, aniline, and various alkaloids.

On gradually adding bromine to a moderately concentrated solution of pure phenol, in a proportion not exceeding that necessary for the reaction $C_6H_5OH + Br_2 = C_6H_4BrOH + HBr$, a white turbidity is produced owing to the formation of the sparingly soluble *monobromophenol* (14 : 1,000). If the solution be dilute, no actual precipitation occurs at this stage. On adding more bromine-water, a formation of *dibromophenol*, $C_6H_3Br_2.OH$, takes place, but often no further precipitation occurs until the bromine added exceeds the proportion—$C_6H_5OH : Br_4$. On further addition of bromine a very bulky precipitate is produced, and when the proportion of phenol is to that of the bromine as C_6H_5OH to

Br_6, the whole is separated as the almost insoluble (1 : 14,300) and characteristic *tribromophenol*, $C_6H_2Br_3OH$. By the action of excess of bromine the hydrogen of the hydroxyl is replaced, in addition to 3 atoms of the phenylic hydrogen, the reaction being $C_6H_5OH + Br_8 = C_6H_2Br_3OBr + 4HBr$. This body, tribromophenol bromide, crystallises in scales, is gradually decomposed by water, and reacts with potassium iodide in acid solution according to the equation:

$$C_6H_2Br_3OBr + 2KI + 2HCl = C_6H_2Br_3OH + 2KCl + 2HBr + I_2.$$

Neither the free iodine nor an excess of potassium iodide has an effect on the tribromophenol. Hence, if it be desired to determine the amount of phenol in an aqueous liquid, it may be effected by adding bromine water in excess, followed by potassium iodide, and then titrating back with a standard solution of sodium thiosulphate in the usual manner. By operating in this way, it is a matter of indifference whether $C_6H_2Br_3OH$ or $C_6H_2Br_3OBr$ be first formed, as by the subsequent treatment with potassium iodide the latter substance is converted into the former.

Tribromophenol. $C_6H_2Br_3OH$. This substance has a very peculiar and persistent odour, melts at 92°, and readily volatilises. It is almost insoluble in water and dilute acid liquids, but is readily soluble in ether, chloroform, carbon disulphide, etc. It dissolves in absolute alcohol, but is precipitated from the solution by a very small quantity of water.

Tribromophenol has marked acid properties. It dissolves in the fixed alkalies and in ammonia, and the latter solution yields on evaporation sparingly soluble crystalline needles of ammonium tribromophenoxide, $NH_4OC_6H_2Br_3$, and from this other tribromophenates may be obtained by double decomposition. The metallic solutions must be perfectly neutral, or a flocculent precipitate of tribromophenol will be obtained. The silver salt forms an orange-yellow flocculent precipitate, the cupric salt is reddish-brown and flocculent, and the lead salt white. The nickel salt is insoluble and dark red, but no precipitate is obtained with solutions of cobalt.

Allen investigated the reactions of the *tribromophenoxides* with a view of finding a means of estimating phenol and cresol in mixtures of the 2, but met with only very partial success, partly owing to the difficulty of preparing a soluble salt of tribromocresol. The following differences were observed in the reactions with neutral

solutions of metallic salts of ammonium tribromophenate and sodium tribromocresolate from coal-tar cresol:

With solution of	Phenol-derivative	Cresol-derivative
Silver nitrate...........	Orange-yellow, flocculent.	Cream coloured, flocculent.
Nickel sulphate..........	Dark red, dissolved on boiling.	Dark red, not dissolved on boiling.
Cobalt nitrate...........	No precipitate...........	Light brown, flocculent.
Calcium chloride.........	No precipitate...........	White, flocculent.
Barium chloride....	White, crystalline, readily soluble in hot alcohol.	White, flocculent not readily dissolved by hot alcohol.
Magnesium sulphate.....	No precipitate...........	White, flocculent.

Estimation of Phenol.—The formation of tribromophenol as a means of determining phenol was first suggested by Landolt, who operated gravimetrically. The method-was greatly improved by Koppeschaar, who devised a volumetric process. This method has been modified by various chemists with more or less advantage. With this process it often happens that the liquid, after being decolourized by thiosulphate, acquires a blue colour on standing. This is said to be caused by bromine (or iodine?) being retained by the oily tribromophenol, and only slowly dissolving in the supernatant fluid. To overcome the difficulty, F. X. Moerck recommends adding a little chloroform toward the end of the reaction. This dissolves the precipitated tribromophenol and the final point of the titration can be more readily observed.

A very simple means of estimating carbolic acid in soap by direct titration with bromine water is given in Vol. 2, page 426, but the process there described is not adapted to yield results of more than approximate accuracy. Very good results are obtainable by the wet bromine process of estimating olefines. In some cases it is preferable to substitute for the bromine water a standard solution of sodium bromate of known strength. A known quantity of the sample to be examined (containing from 0.2 to 0.5 of phenol) is introduced into a stoppered flask, together with a solution of potassium bromide and some dilute hydrochloric acid, and the liquid then diluted to about 100 c.c. with water. A known volume of the standard solution of sodium bromate is then run in, sufficient being used to ensure a permanent reddish colouration due to excess of bromine. The solution should contain 15.1 grm. of sodium bromate per litre.

The flask is then closely stoppered, well shaken, and allowed to stand at rest for half an hour to ensure the completion of the reaction. By the reaction $5KBr + NaBrO_3 + 6HCl = 5KCl + NaCl + 3Br_2 + 3H_2O$, bromine is set free and acts on the phenol. A solution of potassium iodide is then added in excess, and the liquid titrated back with a decinormal solution of sodium thiosulphate (24.8 grm. of the crystallised $Na_2S_2O_3$ per litre), each 1 c.c. of which represents 0.008 grm. of bromine in excess of that which has reacted with the phenol, 0.094 grm. of which causes the disappearance of 0.480 grm. of free bromine, or as much as will be liberated by 10 c.c. of the sodium bromate solution. Instead of preparing a standard solution of sodium bromate, it is preferable to compare the sample to be tested with one of pure phenol.

Titration in carbon disulphide solution is not applicable to the estimation of phenol, the proportion of bromine required being much less than corresponds to the formation of tribromophenol, apparently owing to the formation of an additive compound. Titration by bromine in aqueous solution may be applied to a number of phenoloid bodies with more or less success, but an extensive series of experiments made in Allen's laboratory by J. C. Belcher gave very disappointing results in many cases, apparently owing to the occurrence of secondary reactions forming quinones, etc.

h. An iodometric method of estimating phenol has been devised by Messinger and Vortmann (*Ber.*, 1891, 2753; Abst. *J. Soc. Chem. Ind.*, 1890, 1070). 3 grm. of the sample are dissolved in a little more than 4 grm. of sodium hydroxide ($C_6H_5HO + 3NaHO$), the solution made up to 500 c.c. 10 c.c. of this solution are now warmed to 60° in a small flask, and decinormal iodine run in until the liquid has attained a deep-yellow colour. The mixture is cooled, acidified with dilute sulphuric acid, made up to 500 c.c., and an aliquot part (*e. g.*, 100 c.c.) titrated with decinormal sodium thiosulphate. The amount of iodine used, calculated to the whole amount of the sample taken and multiplied by 0.1235, gives the phenol present.

Method of Estimation of Phenol, given in United States Pharmacopœia (eighth revision, 1900).

Dissolve 1.556 gm. of the phenol to be valued in a sufficient quantity of water to make 1,000 c.c. Transfer 25 c.c. of this solution (containing 0.0389 gm. of phenol) to a glass-stoppered bottle having a capacity of about 200 c.c., add 30 c.c. of N/10 bromine V. S., then 5 c.c.

of hydrochloric acid, and immediately insert the stopper. Shake the bottle repeatedly during half an hour then remove the stopper just sufficiently to introduce quickly 5 c.c. of an aqueous solution of potassium iodide (1 in 5), being careful that no bromine vapour escapes, and immediately stopper the bottle. Shake the latter thoroughly, remove the stopper and rinse it and the neck of the bottle, and then add 1 c.c. of chloroform and shake well. Add, from a burette, N/10 sodium thiosulphate V. S. until the the iodine tint is exactly discharged, and does not reappear after thorough agitation. Note the number of c.c. of N/10 sodium thiosulphate V. S. consumed (which should not exceed 6 c.c.). The percentage of absolute phenol is found by subtracting the number of c.c. of N/10 sodium thiosulphate V. S. used, from 30 (the number of c.c. of bromine V. S. originally added), and multiply the remainder by 4.

A method for estimation of phenols, devised by S. B. Schryver (*J. Soc. Chem. Ind.*, 1899, 553), is based on the fact that sodamide, $NaNH_2$, reacts with hydroxides according to the following equation:

$$NaNH_2 + C_6H_5OH = NH_3 + C_6H_5ONa.$$
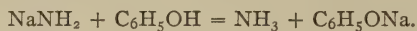
For each molecule of hydroxyl decomposed 1 molecule of amine is liberated. The process consists in bringing an excess of sodamide into a solution of the phenol, using a solvent upon which the reagent has no action. Benzene free from thiophene has been usually employed.

About 1 grm. of sodamide is finely ground, washed 2 or 3 times by decantation with pure benzene, and introduced into a 200 c.c. flask, connected with an inverted condenser. About 60 c.c. of benzene are added, and the mixture is then boiled on a water-bath, while a current of air free from moisture and carbon dioxide is drawn continuously through the separating funnel, the lower end of which dips below the liquid. The boiling and aspirating are continued for 10 minutes, to draw off the last traces of ammonia which adhere to the amide. 20 c.c. of normal sulphuric acid are introduced into the absorption bottle. The weighed portion of the sample, dissolved in about 6 times its weight of benzene, is placed in the bulb of the separator funnel and the solution allowed to drop slowly into the mixture of sodamide and benzene, which is kept boiling continuously and connected with an aspirator. As soon as all the solution has been added, the funnel is washed with a little benzene, and air drawn through the appara-

tus until no ammonia remains unabsorbed. 1.5 hours are generally necessary for this, as ammonia is held rather obstinately by benzene. At the end of the operation the excess of acid is determined by titration (methyl-orange was generally used as an indicator).

To obtain accurate results the materials used and the apparatus must be free from moisture. Sufficient benzene must be used to hold the sodium compound in solution, and it must be free from sulphur compounds. A liberal aspiration of air should be employed. No particular advantage results from substitution of toluene or xylene for benzene. The number of c.c. of normal sulphuric acid required to neutralise the ammonia produced by 1 grm. of the phenol is designated by the author of the process as the "hydroxyl value."

Schryver found fused sodium acetate to be the most suitable drying agent for phenol. The process is applicable in the presence of many hydrocarbons which would act on bromine or iodine, but do not act on sodamide. It may also be employed for determining the proportion of water in phenols, and for estimation of phenols in certain essential oils.

Riegler (*Chem. Centr.*, 1899, 322) has described a method of estimating phenol based on its reaction with paradiazonitraniline to form a soluble red diazo-compound of the formula $C_6H_4NO_2N_2C_6H_4ONa$. On strongly acidifying the solution with dilute sulphuric acid the corresponding diazo-acid separates practically quantitatively, and may be weighed after drying at 100°. The process is also applicable to thymol, guaiacol, etc., but is not available in presence of ammoniacal salts and amines.

A toxicological examination for phenol is not infrequently necessary, owing to the numerous instances in which poisoning has ensued from the accidental administration of the substance internally. In such cases the mouth and esophagus are commonly white, soft, and corroded, but are sometimes found hardened and shrivelled.

The stomach is usually white, contracted, thickened, and shrivelled, but is sometimes intensely congested, with destruction of the mucous membrane. Occasionally, no abnormal appearance is observable. The intestines are usually thickened and congested. The bladder is generally nearly empty; any urine present will have a dark colour.

In testing animal matters for phenol the odour is a most valuable indication. For the recognition of the poison the suspected matters

are cut up and well shaken with water acidified with sulphuric acid. The liquid is then distilled as long as bromine water renders the distillate milky, and the tests for phenol applied to the distillate. The characters of most service are: the odour; the reactions with ferric chloride, sodium hypochlorite, and bromine; and the property of coagulating albumin.

The distillate obtained as above is concentrated by shaking with ether, separating the ethereal layer, and examining the residue of its evaporation; when the amount of phenol is very small, the ether should be shaken with a little dilute sodium hydroxide, the alkaline liquid concentrated, and exactly neutralized by dilute sulphuric acid before applying the foregoing tests.

In cases of suspected poisoning it must be remembered that phenols exist normally in minute quantity in urine, and are formed in small quantity during putrefaction.

COMMERCIAL CARBOLIC ACID.

The better varieties of commercial phenol are well represented by the articles manufactured by F. C. Calvert & Company. Their "No. 1 Carbolic Acid," in the form of colourless crystals, may be regarded as chemically pure and absolute, and free from homologous phenols, the proportion of which gradually increases in the lower grades till the dark liquid known as "No. 5 Carbolic Acid" consists chiefly of *cresylic acid*, with smaller proportions of *higher homologues*. A preparation known as "Carbolic Acid No. 4," containing about 95% of phenols, is much used as a general disinfectant.

In addition to containing water and homologous phenols, the lower grades of commercial phenol are often largely adulterated with *neutral tar oils* ("naphthalene oils") which are of little value as antiseptics.

According to Allen the various modifications of the bromine process of estimating phenols are ill suited for the examination of commercial carbolic acid and its preparations, owing to the fact that ortho- and para-cresol form only dibromo-derivatives. This fact, together with the difference in the molecular weights of phenol and its homologues, renders the results of little quantitative value, unless carbolic acid of the same quality as the sample be used as a standard of comparison. Although, as stated above, the term "carbolic acid" has been extended commercially so as to include products consisting

substantially of cresylic acid or still higher homologues of phenol, it is straining its legitimate signification to apply it to products in which real carbolic acid is conspicuous by its absence. The inexact description becomes still more objectionable when the article is purposely mixed with neutral tar oils, or other hydrocarbons of little direct value as antiseptics. This has been practised to an enormous extent, "carbolic acid" and "carbolic powders" sold to corporations and other sanitary authorities affording a fertile field for the operations of the blender.

For the approximate estimation of *tar oils* in crude carbolic acid the following method has been used: Introduce 10 c.c. of the sample into a graduated tube, and add gradually, noting the effect produced, 4 times its volume of a 10% solution of sodium hydroxide free from alumina. Then close the tube and agitate well. The coal-tar acids will be completely dissolved by the alkaline liquid; while, on standing, the neutral oils will form a separate stratum above or below the other, according as the admixture consisted of the light or heavy "oil of tar." The volume occupied by the oily stratum at once indicates the extent of the adulteration. After noticing whether the tar oils are light or heavy, a volume of petroleum spirit or benzene equal to that of the sample taken may be advantageously added. Its employment facilitates the separation of the oily stratum and renders the reading of its volume more easy and accurate. Of course, the volume of petroleum spirit or benzene used must be deducted from that of the total oily layer. The most accurate method, however, is one in which the oil is distilled to avoid the separation of tarry matters (see page 307).

If the liquid be subsequently acidified with dilute sulphuric acid and shaken, the layer that separates will contain the phenol, and its measure deducted from that of the original sample (after allowing for the volume of the hydrocarbon added) will give the amount of water in the sample.

When a more accurate estimation of the neutral oils is required, and there is sufficient of the sample at disposal, the modified process described in the section on "Creosote Oils" may be used with advantage. The sp. gr. of crude phenol at the ordinary temperature should be between 1.050 and 1.065. If less, it is suspicious. In presence of light tar oil the sp. gr. is often as low as 1.045 or 1.040.

The estimation of the *water* in crude phenol is best effected by distilling a known quantity of the sample with xylol or petroleum naphtha boiling between 149° and 232°, collecting the distillate

in a graduated tube, and noting the volume of the aqueous portion. The results are from 0.3 to 0.5% too low. The inferior grades of crude carbolic acid contain the smallest proportion of water. The following method of assaying crude phenol with a view to ascertaining its quality and the approximate proportion of crystallisable phenol contained in it is due to the late Chas. Lowe, and is largely employed by manufacturers: 1,000 grains or 100 c.c. of the sample are placed in a retort (without any special condensing arrangement), and distilled, the liquid which passes over being collected in graduated tubes. Water first distils and may be measured, and is followed by an oily fluid. When 10% by volume of the latter has been collected, the receiver is changed. The volume of *water* is then read off. If the oily liquid floats on the water, it contains *light oil of tar*. It should be heavier than water, in which case it may be regarded as hydrated acid containing about 50% of phenols. The next portion of the distillate consists of anhydrous phenols, and when it measures 62.5% the receiver is again changed. The residue in the retort consists wholly of cresols and higher homologues. The 62.5% of anhydrous phenols contains variable proportions of carbolic and cresylic acids. These may be approximately determined by ascertaining the solidifying point, which should be between 60° and 75° F. (15.5° and 24°). Having ascertained this temperature, a mixture of pure carbolic and cresylic acids is made in such proportions as to have the same solidifying point. This must be adjusted by trial, or a series of standard specimens may be prepared. The exact point of solidification can be more sharply read if a minute fragment of crystallised carbolic acid be added to induce the commencement of the change of state; or the sample may be solidified, and the liquefying point noted.

Many qualities of crude carbolic acid now contain a comparatively small proportion of light oils (5 to 6%), and hence a notable quantity of phenol is lost in the 10% first distilled. This raises the proportion of cresols in the 62.5% next collected, and hence a product is obtained having too low a solidifying-point. A preferable plan of assaying the second and third qualities would probably be to reject all that passes over below 185°; then distil to 190° or 195°, and take the volume and solidifying-point of this fraction. For No. 1 quality, with 62 1/2% of distillate crystallising above 70° F., only the portion passing over below 180° to 182° should be rejected. About 12% of water may distil from this kind of acid, though the proportion ranges from 10 to 17%, and

also 10% of neutral oils may be present. By stipulating that a sample should contain a certain proportion of anhydrous phenols (exclusive of neutral oils as estimated by soda) distilling below a given temperature and having a definite solidifying-point, a more accurate knowledge of the product would be obtained. The quality of the sample might be also simply expressed in units of anhydrous phenols solidifying at a certain fixed temperature.

The mixtures of phenols from shale tar and blast-furnace creosote are liable to be sold for crude carbolic acid. They may be distinguished from the coal-tar product, as described on page 316.

Crude Carbolic Acid.—These include such products as "100% dark," "100% straw," "90% straw" and fraction acids; the latter are carbolic oils containing various amounts of tar acids. None of these products are supposed to be essentially true carbolic acid or phenol, and some are largely cresylic acids.

The acids are judged by their colour and odour. Pyridine frequently occurring with the carbolic fraction is found in the crude acids.

Soda Test.—Qualitatively this test is applied to the 100% products by shaking the acid with several volumes of 10% sodium hydroxide. Practically nothing should separate or all should dissolve in the case of acids of straw colour; or, better, with dark colour 100% acids there may be some separation.

The sp. gr. test at 15° is a means of determining the relative amount of phenol and cresols. Higher sp. gr. indicates phenol, low indicates cresol. Distillation of 100 c.c. shows the relative amounts of phenol and cresol.

There is no published way of determining the absolute amount of crystal phenol in the crude acids, although some companies producing these products on a large scale have methods which they have worked out by using standard mixtures of phenol and cresols.

Fraction Acids.—"15%," "25%," "50%," "95%," etc. They are sold with and without a guarantee that they will not deposit naphthalene if held at 0° for 1 hour. The first quality have the guarantee. Tar acids are estimated as follows: 25 c.c. are distilled in a small flask to dryness, diluted with benzol in stoppered cylinder to 25 or with second-quality oils to 50 c.c. (in this case the result found is multiplied by 2). 10 c.c. of distilled oil is taken in a tube graduated from zero to 20 c.c., and 10 c.c. of 10% sodium hydroxide added. As the soda gains in volume consider the gain from 10 c.c. as

tar acids in the sample.   If the division line between the 2 liquids
stood at 13 c.c., it would mean that there was 20% of tar acids
in the sample.

An alternate method that gives different results consists in weighing
some of the sample, extracting with several amounts of diluted
alkali (in some cases 5% and in others 10% sodium hydroxide) until no
more can be extracted, decomposing the soda salts formed with mineral
acid and extracting with ether until all is taken up.   The residue in
the flask after evaporating off the ether is the amount of tar acids.
While this method is the more accurate the first method is usually
depended on in the works, and the method of analysis should be selected
with reference to the understanding upon which the acids are bought
and sold.

"No. 5 Acid" Cresol.—This acid should be water-white, contain no
water and only traces of neutral oil (when treated with sodium
hydroxide solution.

There are no requirements as to b. p., although a distillation record
can be made as under Fraction acids (see page 307).

LIGHT TAR OIL.

Sp. gr. is taken at 15° in Westphal balance or other suitable manner.
Water is sometimes found and is noted in the distillation.

Distillation in Ordinary Distilling Flask.—The temperature at
each 10 c.c. is noted.   Tar acids are then extracted, the shrinkage in
volume being determined in a tube measuring 100 c.c. from the
stop-cock at the bottom to a point near the top, in which a glass
stop-cock is fitted.

CARBOLIC ACID DISINFECTING POWDERS.[1]

A variety of disinfecting powders are now made, which owe their
efficacy chiefly to the fact of their containing a greater or smaller % of phe-
nols.   It is probably the case that these carbolic powders are not as much
used as they were when the earlier editions of this work were published.
Liquid preparations are much more used for animal disinfection and
more definite synthetics are used for human medicinal purposes, but
the methods of estimation of the active agents of these powders apply

[1] The examination of liquid antiseptic preparations containing phenols and cresols
is described on page 318 *et seq.*

to a sufficiently large number of preparations to retain the few para-
graphs here devoted to this purpose. In some cases the base of the
powder is slaked lime, but the so-called "carbolate of lime" is of little
value for antiseptic purposes. "Macdougall's Disinfecting Powder,"
the oldest preparation of the kind, was made by adding a certain pro-
portion of crude carbolic acid to a crude calcium sulphite, prepared by
passing sulphurous acid gas over ignited limestone. Sulphurous acid
is introduced into other powders by the direct addition of a solution of
calcium hydrogen sulphite. "Calvert's Carbolic Acid Powder" is
made by adding carbolic acid to the siliceous residue resulting from
the manufacture of aluminum sulphate from shale or kaolin. Calcium
sulphate is likewise a suitable absorbent, and kieselguhr has been used
for the stronger powders. The use of peat as an absorbent of carbolic
acid has been patented by West Knights and Gall, while Allen and
Angus have proposed the use of blast-furnace slag. Limestone is also
used. The use of spent gas-lime has been patented by Austin. A
mixture of bleaching powder and phenol has also received protection.
Macdougall Brothers have employed soluble salts as absorbents, the
resultant powder being more readily removed and less liable to choke
up drain-pipes than the preparations commonly employed. A step
in the same direction is *borophenol*, prepared by absorbing carbolic
acid by dried borax.

Good carbolic acid powders contain at least from 12 to 18% of
crude carbolic acid, but higher strengths are obtainable. As much
as 50% is absorbed by kieselguhr. All carbolic powders are liable to
lose 1 or 2% by volatilisation. Some powders in the market contain
but 5 or 6% of total oils, of which less than half is really carbolic and
cresylic acids, the remainder being neutral tar oils.

For the estimation of the phenols and tar oils in disinfecting powders
having a siliceous base, and in others containing the phenol in the free
state, 50 grm. should be exhausted with ether in a Soxhlet-tube or
similar arrangement. The ethereal solution is then agitated with
about 20 c.c. of a 20% solution of sodium hydroxide, more or less than
this quantity being employed according to the percentage of phenols
supposed to be present in the powder (and about 1 c.c. of the reagent
being used for every 1% of phenols in the sample). The ethereal
layer is separated, and the alkaline liquid again shaken with ether,
which is separated as before, and added to the main quantity. The
united ethereal solutions are shaken with some sodium hydroxide

solution, to dissolve out any phenols which may have escaped the previous treatment. The ether is then driven off by a gentle heat and the residual oils are weighed. The united alkaline liquid is boiled down in a flask to a small bulk (10 c.c.), and transferred to a burette or other suitably graduated tube, where it is treated with diluted sulphuric acid (1 : 3) in quantity sufficient to render the liquid distinctly acid to litmus after agitation. When the liquid has stood for some time and is *thoroughly cold*, the layer of separated phenols is measured. Each c.c. weighs about 1.050 grm., so that an addition of 5% to the measure gives the correct weight. The results are fairly accurate, but generally below the truth, owing chiefly to the solubility of phenols. Hence the liberation of the phenol should be effected in a liquid as concentrated as possible.

In cases in which the characters of the separated phenols suggest the presence of fatty acids, resin, or other foreign matter, the contents of the burette should be transferred back to the flask, diluted with water, and distilled. The phenols readily pass into the distillate, whereas any fatty or resin acids will remain in the retort.

In the case of powders made with lime, or others in which the phenols exist in combination, the method of direct extraction with ether or other solvent does not give accurate results. For the determination of the crude carbolic acid in such powders, the disinfectant value of which is very doubtful, the following method may be employed: 50 grm. of the sample should be mixed in a large mortar with 5 c.c. of water. Strong sulphuric acid, previously diluted with an equal bulk of water, is then added very gradually, a few drops only at a time. After each addition the whole is well mixed together with a pestle. The addition of the acid, which should extend over some hours to avoid sensible rise of temperature, is continued until a minute fragment of the well-mixed contents of the mortar shows an acid reaction when placed on a piece of litmus-paper and moistened with water. If the mixture be pasty, sufficient sand is added to cause it to granulate, and the mortar is then covered up and left for some hours. By this method the lime, sulphuric acid, and water form hydrated calcium sulphate and the phenols are liberated. The product is then exhausted with ether in a Soxhlet-tube or similar contrivance.

Whether isolated by the extraction or the distillation process, the crude carbolic acid obtained should be further examined for *neutral tar oils,* which not infrequently constitute the greater part of the so-called " car-

bolic acid" of disinfecting powders. For their detection, the test with dilute sodium hydroxide will usually be found sufficient. In other cases the crude carbolic acid should be treated with twice its measure of a 20% sodium hydroxide solution (1.2 sp. gr.), any undissolved oils separated, and the alkaline solution shaken with ether to remove any neutral oils still remaining dissolved. The ethereal layer is separated, added to the neutral oils previously obtained, the ether driven off by a gentle heat, and the residual neutral oils or naphthalene measured or weighed. The alkaline solution of the phenols is boiled in a small flask to drive off the ether, and acidulated in a narrow, graduated tube or a burette with diluted sulphuric acid (1:3), and the layer of separated phenols is measured.

The *sulphurous acid* contained in certain disinfecting powders may be estimated by stirring 1 grm. of the sample in a mortar with a small quantity of distilled water free from air, and decanting the liquid into a flask containing 50 c.c. of the ordinary N/10 solution of iodine and about 250 c.c. of water. The residue in the mortar is repeatedly treated with fresh quantities of water, the resultant liquids being transferred to the flask, and finally the undissolved powder is rinsed in. Very dilute hydrochloric acid is next cautiously added to the contents of the flask, until the reaction is distinctly acid, when the excess of iodine is estimated by titration with N/10 thiosulphate in the usual way. Each c.c. of N/10 iodine reduced represents 0.0032 grm. of SO_2.

CRESOLS. CRESYLIC ACIDS.

Methylhydroxybenzenes. $C_7H_8O = C_6H_4(CH_3)(HO)$.

Cresol being formed by the substitution of 2 of the hydrogen atoms in benzene, by methyl and hydroxyl, respectively, 3 isomeric forms are possible, all of which occur in the crude cresylic acid from coal-tar. Any modification of cresol can be obtained pure by dissolving the corresponding form of toluidine and an equal weight of sulphuric acid in about 30 parts of hot water. An aqueous solution of potassium nitrite is next added in quantity sufficient for the reaction:

$$C_7H_7.NH_2 + KNO_2 + H_2SO_4 = C_7H_7.OH + KHSO_4 + H_2O + N_2.$$
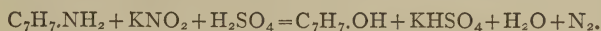
The liquid is then saturated with common salt or sodium sulphate, allowed to cool, and the layer of cresol separated and purified by dis-

tillation.   The following table shows some distinctions between the cresols, according to various observers:

	Orthocresol	Metacresol	Paracresol
M. p. °..................	30; 31–31.8	4; 3–4	36; 36–37
B. p. °..................	188; 190.8	201; 202.8	201.8; 198–199
Sp. gr. at 0°............	1.0578	1.0498	1.0522
Coefficient of expansion...	.0.00072	0.00078	0.00086
Solubility in water........	1 in 40	1 in 200	1 in 55
Highest bromo-derivative.	Br$_2$; m. p. 52°	Br$_3$; m. p. 82°	Br$_2$; m. p. 49°
Highest nitro-derivative ..	(NO$_2$)$_2$; m. p. 85.8°	(NO$_2$)$_3$	(NO$_2$)$_2$; m. p. 82.5

The m. p. and b. p. recorded by different observers are not in very perfect concordance.   The sp. gr. and coefficients of expansion are figures by Pinette (*Annalen*, **243**, 3), and apparently refer to the liquid cresols, which exhibit, in a marked manner, the phenomenon of super-fusion.   The "highest bromo-derivative" means the most highly brominated substitution compound which does not react with potassium iodide.   Thus, in the case of phenol it would be $C_6H_2Br_3.OH$, not $C_6H_2Br_3.OBr$.

Metacresol forms a tribromo- and trinitro-derivative, whereas the ortho- and para-forms give only disubstitution products.   According to Ditz and Cedivoda (*Zeit. angew. Chem.*, 1899, 873, 897), ortho- and paracresol form tribromo-derivatives, but these are converted into the corresponding dibromocresols by potassium iodide. Metacresol forms $C_7H_4Br_3OBr$, which is converted into $C_7H_4Br_3OH$ by potassium iodide.

When fused with potassium hydroxide, the cresols are converted into the corresponding forms of hydroxybenzoic acid (see under Salicylic Acid).

The United States Pharmacopœia describes cresol and gives tests as follows:

A colourless or straw-coloured refractive liquid, having a phenol-like odour, and turning yellowish-brown on prolonged exposure to light.

Sp. gr. 1.032 at 25° (77° F.).

Cresol is soluble in 60 parts of water at 25° (77° F.); miscible in all proportions with petroleum benzin, alcohol, benzene, ether, and glycerin; miscible with alkali hydroxide solutions.

It boils at from 195° to 205° (383° to 401° F.).

If 1 c.c. of cresol be mixed with 1 c.c. of an aqueous solution of sodium hydroxide (1 in 10), it should dissolve with no appreciable liquid residue (absence of, or limit of, hydrocarbons).

If 1 c.c. of cresol be mixed with 1 c.c. of glycerin, a clear solution should be produced, from which, on the addition of 1 c.c. of water, the cresol should completely separate (absence of, and distinction from, phenol).

Orthocresol was formerly supposed to form a hydrate of the composition $C_7H_8O + H_2O$, which is liquid at ordinary temperatures, has a sp. gr. of 1.06, and is soluble in ether and alcohol in all proportions.   According to H. Nördlinger, 100 parts of cold water dissolve 3 parts of orthocresol; but Gruber gives the solubility as 2.5% by volume: the figure for metacresol being 0.53; for paracresol, 1.8 for mixed coal-tar cresols, 2.55; for mixed cresols from toluidine, 2.2; and for phenol, 6.0%.   The last figure is certainly too low.

Nördlinger states that orthocresol is less poisonous and corrosive than its isomers, and can be produced with ease in large quantities and at a lower price than the other forms.   A 1% aqueous solution of orthocresol is not decomposed or rendered turbid by acids or neutral salts, does not affect the skin or render the hands slippery or numb, and has no action on metals.   Solutions containing 0.25 to 1% are stated to have an antiseptic power equal to solutions of phenol containing from 2 to 5% of phenol.

According to Nördlinger, the 3 modifications of cresol may be distinguished by their behaviour with ammonia.   When a few drops of orthocresol are shaken with a few c.c. of ammonia solution the mixture becomes bluish on standing—like a dilute solution of cupric sulphate—but after a few days it acquires a deep indigo-blue colour and becomes opaque.   Paracresol, when treated similarly, gives a transparent pale yellow liquid.   Metacresol also gives a transparent liquid, which at first has a faint steel-blue colour, afterward becoming bluish, but the tint is distinguishable from the deep indigo-blue yielded by orthocresol.

F. Raschig (*Zeits. angew. Chem.*, 1900, **31**, 795) has found a means of separating metacresol from para- and orthocresols.

The method is based upon the fact that upon nitration 1 grm. of metacresol yields almost exactly 1.74 grm. of trinitrocresol, whereas ortho- and paracresol are destroyed.   10 grm. of the cresol are weighed into a small Erlenmeyer flask, and 15 c.c. of sulphuric acid (66° B.) are added.   The flask is heated for an hour in a steam oven.   The contents are then poured into a flask of about a litre capacity, and cooled under the tap.   90 c.c. of nitric acid (40° B.) are poured into

the small flask, shaken around, and then rapidly transferred to the large flask. The latter is then shaken round vigorously for about 20 seconds until solution is complete. After about a minute an energetic action commences, which lasts 5 minutes. After standing a further 5 minutes, the flask is emptied into a basin containing 40 c.c. of water, and is rinsed out with another 40 c.c. The trinitro-m-cresol, which separates out, is filtered off, dried at 95°–100°, and weighed. The results obtained are not affected by the presence of even large proportions of xylene or ortho- and paracresol.

10% of phenol also does not effect the result, but if a larger proportion be present, some picric acid separates with the trinitrocresol.

Estimation of metacresol in mixtures of cresols according to H. Ditz (*Zeits. angew. Chem.*, 1900, **42**, 1050):

About 1 grm. of the anhydrous cresol mixture is weighed out, dissolved in water with the aid of some sodium hydroxide, and the solution diluted to 250 c.c. 2 portions of 25 c.c. each are transferred to well stoppered flasks, and decomposed with a sufficient quantity of Koppeschaar's bromide-bromate solution, and 10 c.c. of hydrochloric acid (1:1). After being shaken for exactly 1 minute, 20 c.c. of a 5% solution of potassium iodide are introduced, the iodine which separates titrated with standard thiosulphate after 1 hour, and the amount of bromine absorbed calculated from the result. The quantity of metacresol is then obtained from the equations

$$x + y = a \quad \text{and} \quad \frac{3\,Br\,x + 2\,Br\,y}{108.08} = b,$$

in which x = the amount of metacresol; y, the sum of the ortho- and paracresol; a, the weight of the total cresols; and b the weight of bromine absorbed, hence:

$$x = a - y = a - \frac{2.2195\,a - b}{0.7397} = \frac{b - 1.4798a}{0.7397}$$

If a cresol mixture contain any traces of water, the latter is removed preferably by heating 5 to 10 grm. of the mixture in a small fractionating flask, and after removal of the water distilling over the cresol. According to the author's experimental results, the accuracy of the method is within 0.5%.

It is not possible to determine separately by this method each of the individual constituents in a mixture of phenol with the 3 cresols, but it suggested that this problem may be solved by a combi-

nation of the Ditz's method with that of Raschig, as given above. The only difficulty is that in the latter the presence of more than 10% of phenol interferes, but this may be obviated by adding to the mixture a known quantity of pure metacresol, or a definite quantity of a cresol mixture which is free from metacresol, so as to reduce the total amount of phenol below 10%.

Cresylic Acid from Coal-tar.—The 3 isomeric cresols are stated by Schulze to exist in gas-tar approximately in the proportions of 35% of orthocresol, 40 of metacresol, and 25% of paracresol. 1:3:5 and 1:2:4 xylenols have been found in the fraction of gas-tar phenols boiling between 170° and 210°. Cresylic acid from gas-tar has a density of 1.039 to 1.044. It closely resembles phenol, but is liquid at common temperatures, far less soluble in water, and boils at a higher temperature. The b. p. of commercial cresol is variable, as it contains more or less phenol and higher homologues. Samples of commercial phenol (even when anhydrous) containing much cresylic acid remain fluid at ordinary temperatures, and are less soluble in water and dilute alkaline liquids than is pure phenol. Cresylic acid resembles phenol in its reaction with ferric chloride. With some samples the blue colouration first produced rapidly changes to brown.

Cresylic acid dissolves in dilute sodium hydroxide solution containing far less alkali than corresponds to the proportion $C_7H_8O:NaHO$, but on adding water 2 layers are formed, the lower one of which closely resembles cresylic acid, but sometimes occupies a considerably greater volume than that of the sample used. When acted on by strong nitric or sulphuric acid cresol gives similar, but not identical, products with those yielded by phenol. With excess of bromine it produces a similar body, but brominated cresol from coal-tar cresylic acid is liquid at ordinary temperatures, whereas the phenol derivative is solid.[1]

The following table shows the chief differences of analytical value existing between phenol and cresol. The statements were personally verified by Allen upon a sample of Calvert's "No. 1 carbolic acid" and a cresylic acid prepared purposely by careful fractional distillation of a sample of Calvert's "No. 5 carbolic acid." The cresylic acid was further purified by dissolving it in sodium hydroxide and agitating the solution with ether to remove naphthalene and other hydrocarbons, the cresol being subsequently

[1] See Allen's paper on Commercial Cresylic Acid, *J. Soc. Chem. Ind.*, 1890, 141.

recovered by addition of acid. If this treatment be omitted, scales of naphthalene, etc., are liable to separate on treating the sample with ammonium hydroxide.

	Phenol	Cresylic acid
M. p..................	Solid at ordinary temperatures; liquefied by addition of water; in both absolute and hydrated condition solidified by freezing mixture.	Liquid at ordinary temperatures; neither absolute nor hydrated acid is solidified by freezing mixture.
B. p................ ..	182°....................	198° to 203°.
Solubility of hydrated acid in cold water.	1 volume in 11............	1 volume in 29.
Solubility in ammonium hydroxide (sp. gr. 0.880) at 15°.	Completely and readily soluble in equal volume; solution not precipitated by addition of less than 2 1/2 volumes of water.	Soluble in equal volume; the solution is precipitated by slight cooling or dilution.
Reaction with petroleum spirit.	Absolute acid is miscible with hot petroleum spirit in all proportions. Miscible with only 1/2 volume of *cold* petroleum spirit; precipitated by greater proportion. With 3 volumes petroleum spirit, bulk unchanged; upper layer contains carbolic acid, which crystallises out on sudden cooling by freezing mixture.	Absolute acid miscible in all proportions. No separation of crystals or liquid produced by suddenly cooling solution in 3 measures of petroleum spirit.
Behaviour with glycerol of 1.258° sp. gr. at 15°.	Miscible in all proportions. One measure of phenol with an equal volume of glycerol is not precipitated on addition of 3 measures of water. In presence of cresylic acid less dilution is possible, 2 volumes of water being the maximum for a sample containing 25% cresylic acid.	Miscible in all proportions. One measure of cresylic acid, mixed with 1 measure of glycerol, is completely precipitated by 1 measure of water.

All the cresols possess antiseptic and disinfectant properties to a greater degree than phenol, metacresol being the most active, but the sparing solubility of all the cresols in water is a serious disadvantage.

From these values it will be seen that cresol is less soluble than phenol in water, ammonia, and glycerol, but it is more soluble in petroleum spirit. According to W. W. Staveley, absolute phenol is soluble in petroleum spirit, but is separated by water. The separation is prevented by the presence of from 20 to 25% of benzene in the petroleum spirit. Anhydrous cresol is also soluble in petroleum spirit, and is separated by water. On adding a saturated solution of calcium chloride, the water, is taken up and the cresol redissolves in the petroleum spirit. The first fraction of neosote behaves like cresol. As a whole, neosote dissolves in petroleum spirit and is not separated by water. Although the above tests suffice for the detection of considerable proportions of cresylic acid in admixture with phenol, they afford no basis for its quantitative estimation, except of the roughest kind. Encouraging results have been obtained by Ewell and Prescott by the use of a 9% solution of sodium hydroxide (*Analyst*, 1888, 237). The best means of even approximately estimating the proportion of cresylic acid present in samples of crude phenol is by fractional distillation.

The following table shows the behaviour of 3 typical samples of *commercial cresylic acid* when distilled in a flask furnished with a dephlegmator:

	Commer-cial	Commer-cial	Once-run
Sp. gr.	1.041	1.049	1.038
Water	trace	8.5	0.5
First drop distilled at	120°	90°	95°
Percentage distilling below 180°	0.2	2.5	0.5
Percentage distilling from 180° to 190°	4.6	4.0	1.0
Percentage distilling from 190° to 195°	56.6	16.5	15.5
Percentage distilling from 195° to 200°	23.0	20.0	36.0
Percentage distilling from 200° to 205°	10.0	16.0	19.5
Percentage distilling from 205° to 210°		9.5	11.0
Percentage distilling from 210 to° 215°		6.0	6.0
Percentage distilling from 215° to 225°		6.6	6.5
Total	96.4	89.5	96.5

A sample of Calvert's "No. 5 carbolic acid," when fractionated in the same manner, gave 6.8% over below 180° (including 5.5% of water), 5.6 between 180° and 186°, 46.8 between 186° and 190°, 28.8 between 190° and 195°, and 7.0 between 195° and 200°; the total over at this temperature being 95.0% by measure. The last 3 fractions distilled had a sp. gr. of 1.0541, 1.0430, and 1.0370, respectively. The gradual decrease of gravity with increase in the b. p. is a constant feature in the fractionation of phenols.

The phenoloids of blast-furnace tar, contained in the "neosote" of commerce are chiefly cresols.

Analysis of Creosote and Cresylic Acid Sheep Dips.

The following methods are taken from Bulletin 107, Bureau of Animal Industry, United States Department of Agriculture. These methods will also apply to a large number of liquid insecticides that contain phenols and neutral oils.

Estimation of Water.—50 grm. of dip is weighed into a 100 c.c. fractionating flask with a moderately high side tube, beyond the exit of which the neck should continue for not more than 1 in., and the flask is connected with a small water-cooled condenser and carefully heated with a smoky flame until oils come over freely and carry no trace of water with them, but the distillation should not be unnecessarily continued. The distillate is received in a properly graduated 25 c.c. cylinder, allowed some time to separate completely, and the volume of water read. The number of cubic centimeters of water multiplied by 2 equals the % of water. Ordinarily the process offers no difficulties. A dip extremely high in rosin may bump and froth over, no matter how carefully heated. In such a case a larger flask is used, and the dip is diluted with about an equal volume of water-free mineral[1] or coal-tar oil. In case separation of the distillate is imperfect, a small measured amount of strong NaCl solution is added from a pipette, and the cylinder is nearly filled with benzol, shaken, and left at rest for some time. The volume of NaCl solution added is of course to be deducted when the reading is taken.

Estimation of Soda and Pyridine Bases.—The method, which is a novel combination and adaption of well-known principles and

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[1] In any case it would probably be well to add a liberal excess of mineral oil, and I have found that a fraction from heavy benzin boiling between 149° (300° F.) and 232° (450° F.) gives satisfactory results. (Amer. Ed.)

processes, depends upon the fact that pyridine bases are alkaline toward methyl-orange, but not toward phenolphthalein. A known weight of dip is shaken in a separatory funnel with ether and water to which a known amount of sulphuric acid has been added. Rosin soap is thus decomposed, and all bases contained in the dip will pass as sulphates into the lower acid aqueous layer which soon separates. The latter is quantitatively removed, and, ignoring acid salts for the sake of simplicity, will contain the substances—

(a)	(b)	(c)
Stage I. Na_2So_4.	H_2SO_4.	$(C_5H_5N)_2H_2SO_4$.
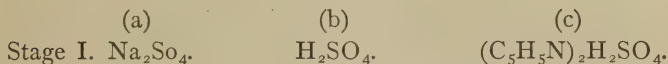
If methyl-orange is now added and the solution titrated to neutrality with standard sodium hydroxide the result will be—

(a)	(b)	(c)
Stage II. Na_2SO_4.	Na_2SO_4.	$(C_5H_5N)_2H_2SO_4$.
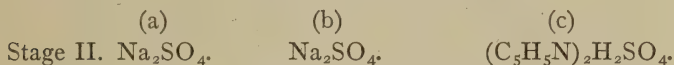
If next phenolphthalein is added and titration with standard caustic soda contained until the solution is neutral to that indicator, the final condition of the solution will be—

(a)	(b)	(c)	
Stage III. Na_2SO_4.	Na_2SO_4.	Na_2SO_4.	C_5H_5N.
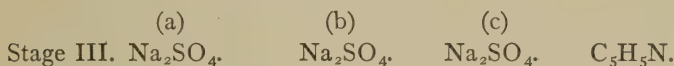
Obviously the amount of sodium hydroxide required to change the solution from Stage II to Stage III will be a measure of the amount of pyridine present, while if the amount of sodium hydroxide added in the whole titration is subtracted from the equivalent in soda of the sulphuric acid originally introduced, the remainder will equal the amount of soda in the dip. Briefly, the amount of soda equivalent to H_2SO_4 (c) measures pyridine; soda equivalent to H_2SO_4 [(a+b+c) − (b+c)] is the soda of the dip. The process is executed in the following manner:

10 grm. of dip is weighed into a 200 c.c. short-stemmed separating funnel, 50 c.c. ether added, exactly 30 c.c. of $N/2$ H_2SO_4 run in from a burette and the funnel shaken. The lower aqueous layer, which now contains the bases, is drawn off completely, together with any insoluble carbonaceous matter which may appear at the junction of the 2 layers. No harm is done if a small amount of the ethereal layer accompanies the insoluble matter in the separation. The ethereal solution remaining in the funnel is next washed 4 times with water, using about 20 c.c. each time. In the first of these washings the funnel should not be shaken, but the water should be drawn off at once, the

object being to wash out the stem of the funnel and so avoid loss of a little acid therein contained.

All the aqueous extracts are united and heated on the steam-bath for expulsion of ether. The liquid is then passed through a wet filter into a 300 c.c. flask, the filter washed with hot water, the flask cooled, filled to the mark, and the contents exactly divided between 2 uniform titrating flasks of about 300 c.c. capacity. To 1 of these portions add methyl-orange, then $N/2$ NaOH till the red tint just disappears, as nearly as can be determined by comparison with the second portion. Then add $1/10$ or $2/10$ of a c.c. more of $N/2$ NaOH to make sure that neutrality has been reached, though much excess must be avoided, else the separation of higher pyridine bases will render the solution turbid.

This first titration is not quantitative, but merely to afford a standard of comparison, by the aid of which the second portion is quantitatively titrated to exact neutrality, after the addition of an equal amount of methyl-orange. The number of c.c. of $N/2$ NaOH used is noted, phenolpthalein added, and the titration continued to the end-point of that indicator. To obtain the % of Na_2O in the dip, subtract the total number of c.c. of $N/2$ NaOH used in the whole titration of the second portion from 15, and multiply the remainder by 0.31. To obtain the % of volatile bases reckoned as pyridine, multiply the number of c.c. of $N/2$ NaOH used between the end-points of methyl-orange and phenolphthalein by 0.79. The only difficulty in the method is the determination of the point of neutrality toward methyl-orange, but a proper use of the standard of comparison will satisfactorily overcome this.

Recent work has indicated that the colouring matters which tend to interfere with the accurate observation of the end-point with methyl-orange may be almost entirely removed from the solution by the use of animal charcoal. Powdered animal charcoal is digested on the steam-bath with dilute hydrochloric acid in sufficient quantity to decompose and dissolve all carbonates and phosphates present, then washed with hot water until the wash-water is free from chlorides, and finally dried and powdered.

In the course of an analysis, after the flask containing the acid extract from the dip has been heated upon the steam-bath until ether has been completely expelled, 1 to 1.5 grm. of the purified animal charcoal are added, and the flask, frequently shaken, is left upon the

steam-bath for 30 to 60 minutes. The contents are then filtered, washed, and titrated as usual. After proper treatment with animal charcoal in this manner the solution will be a pale green in colour, possessing none of the muddy yellow tint which tends to obscure the end-point with methyl-orange.

Experiments have thus far failed to show that any inaccuracy is introduced into the method by the use of animal charcoal in the manner described.

Phenols.—50 grm. of dip are weighed into a 500 c.c. round-bottomed flask, 20 c.c. of $1:3$ H_2SO_4 are added, and the phenols are distilled off with steam. The flask will require no heating if a rapid current of steam is passed into it, but may with advantage be packed in cotton or felt. Obviously the apparatus must be so set up and the distillation so conducted that particles of rosin may not be mechanically carried over by the current of steam. Toward the end of the distillation any naphthalene in the condenser is melted out by shutting off the water for a few minutes, or if separated earlier in sufficient quantity to threaten stoppage of the condenser tube, distillation is interrupted while hot water is run through the condenser. The distillate is received in a litre flask approximately marked for each 100 c.c. capacity and joined to the condenser by a cork which is pierced by a small glass tube connected to a small **U**-tube containing a little dilute sodium hydroxide. The latter acts as a trap to prevent any loss of the distilled phenols. Distillation is continued until 1 or 2 c.c. collected in a test-tube give no reaction with any appropriate reagent for phenols, such as ferric chloride. A volume of 800 c.c. is ample in nearly all cases.

A supply of benzol should be prepared by shaking a good grade of benzol with dilute sulphuric acid, then with dilute sodium hydrozide 2 or 3 times, and then passing through a dry filter. A small washbottle containing some of this benzol will be found very useful for rinsing the necks of separatory funnels, etc. Of this purified benzol 150 c.c. are measured out conveniently at hand, the contents of the **U**-tube and 5 c.c. of $1:1$ H_2SO_4 are added to the distillate, and the latter is shaken up and poured into a separatory funnel of 1,500 c.c. capacity, the flask being rinsed out with successive portions of the 150 c.c. benzol. When all is in the funnel 25 grm. of clean sodium chloride are added for each 100 c.c. of distillate, and the funnel is well shaken for 5 minutes and left at rest 1/2 hour. The aqueous layer is then run off

slowly and completely, the funnel being allowed to stand until there is no further separation. The benzol solution of phenols and hydrocarbons is transferred to a 500 c.c. Erlenmeyer flask, while the aqueous portion is poured back into the separating funnel and extracted twice more in the same way, 100 c.c. of benzol being used each time. The funnel should always be gently handled after the aqueous portion has been drawn off, to prevent any impurities from the sodium chlorid which have deposited upon its sides from becoming mixed with the benzol solution. The 3 benzol extracts are united in the Erlenmeyer flask, 15 c.c. of pure sodium hydroxide solution, 1 : 2, is added, and the contents of the flask are subjected to a rotatory motion for some time in order that the phenols may be taken up by the sodium hydroxide as completely as possible.

After the addition of a few grains of sand the flask is immersed in a water-bath, connected to a condenser, and all but 40 to 50 c.c. of the benzol distilled off. With the aid of a wash-bottle containing water and provided with a fine jet, only a small portion of water being used at a time, the contents of the flask are next carefully washed into a 150 c.c. separatatory funnel. With proper manipulation the flask should be completely washed when the volume of aqueous portion in the separatory funnel amounts to not more than 50 c.c. 10 c.c. of strong sulphuric acid (100 c.c. pure concentrated H_2SO_4 to 120 c.c. water) are next slowly introduced with gentle rotation of the funnel, the addition of acid being interrupted and the funnel cooled whenever it becomes unpleasantly warm to the hand. 2 or 3 drops of methyl-orange are now added; and if on mixing the contents of the funnel the lower layer does not acquire a pink colour, the addition of acid is continued until acidity is assured. Sufficient benzol is then added to make the 2 layers in the funnel approximately equal in volume, the funnel is thoroughly shaken and, with loosened stopper, left at rest for 2 hours. After that time the aqueous layer is slowly and completely run out, the analyst making sure that on longer standing no more will drain down from the sides of the funnel. The benzol solution of phenols is then ready to be transferred to the measuring tube.

The measuring tube consists of a glass-stoppered pear-shaped bulb of about 100 c.c. capacity, joined at its tapering end to a tube about 1 foot long and of a capacity of 25 to 30 c.c. This tube is accurately graduated to contain 25 c.c. at 20° in divisions of 1/10 c.c. (see Fig. 8).

The apparatus is cleaned thoroughly with soap powder and hot

water, and dried, best spontaneously, though alcohol and ether may be used if pure. Perfect cleanliness is essential to insure a properly shaped meniscus. Between 15 and 16 c.c. of sodium hydroxide solution, 1:3, is brought into the tube with a pipette. The sodium hydroxide should not be allowed to come in contact with the interior of the bulb or the upper part of the tube. After a few moments about 1 c.c. of benzol is added, and after waiting a little the height to the top of the now almost flat meniscus is noted. The benzol solution of phenols is next transferred from the separatory funnel to the tube, care being used to avoid mixing with the soda; the separatory funnel is washed out with a little benzol, which is also transferred to the tube, and the height of the meniscus is again noted. The latter may often be obtained more accurately at this point. The tube is then stoppered, vigorously shaken for 3 minutes, and set aside for at least 3 hours. An occasional rapid rotation of the tube between the palms of the hands will insure a complete separation of the layers. Each c.c. increase in volume of the sodium hydroxide solution may be taken to represent 1 grm. of phenols. All readings of the tube should be taken at the top of the meniscus and at a temperature as near 20° as practicable.

This method of treating the distilled phenols is essentially that of Spalteholz (*Chem. Zeit.*, 1898, **22**, 58–59), though the details of its execution were not imparted in the original communication and had to be worked out independently.

From certain experiments it seems possible that a continuous extraction apparatus[2] may be successfully employed to extract phenols from the aqueous distillate of the dip, using benzol as the solvent, and introducing sodium hydroxide solution into the distillation flask of
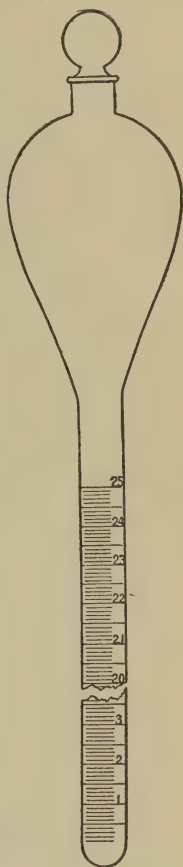
FIG. 8.[1]

[1] The use of this cut was kindly granted by the Bureau of Animal Industry, U. S. Dept. of Agriculture.
[2] Forms of extraction apparatus may be obtained of all ground-glass connections for extracting aqueous liquid, with solvents lighter than water and solvents heavier than water, or in the usual way as a Soxhlet extractor depending upon the use of special attachments for, the several purposes intended. (Amer. Ed.)

the apparatus at the beginning of the operation to retain the extracted phenols. When the extraction is completed the small flask of the apparatus will contain all the phenols, dissolved in a limited amount of sodium hydroxide solution and overlaid by about 50 c.c. of benzol. The contents of the flask may then be brought readily and completely into a separatory funnel and acidified in the usual manner. Certain exigencies of the work in this laboratory[1] have rendered somewhat inconvenient at the present time a practical test of this method of procedure in the routine examination of dips submitted for analysis.

Determination of Rosin Acids.—Resins in general have been shown to contain at least 3 different classes of bodies (Allen, Vol. 4): (1) resin acids or anhydrides, (2) esters of these or similar acids, (3) indifferent neutral bodies, perhaps hydrocarbons. Common rosin, or colophony, contains, according to Allen (Id., p. 25), between 83.4 and 93.8% of free rosin acids or anhydrides. The remaining 6 to 17% consists of neutral bodies, soluble in ether and not extracted from ethereal solution by aqueous sodium hydroxide, and accordingly there would seem to be no practicable means of distinguishing and separating them from the coal-tar hydrocarbons of the dip. Apparently, then, the analyst must be content with a determination of the amount of rosin acids present, which will represent about 9/10 of the amount of rosin actually used in manufacturing the dip. Either a gravimetric or a volumetric method may be employed.

Owing to the degree of uncertainty attached to the exact combining equivalent of the rosin acids in each particular dip, the gravimetric method has an indubitable advantage in point of accuracy when properly carried out. But as a matter of fact the combining equivalents of a considerable number of rosin acids obtained from different dips in the gravimetric way in the course of analysis have been found to vary very little, not enough in any case to cause a possible error of 0.5% in the analysis of a dip of ordinary constitution. Moreover, in view of the difficulty of completely separating hydrocarbons from rosin acids, as is necessary in the gravimetric method, it is probable that the ordinary analyst without considerable practice in this particular operation will obtain quite as accurate results by the volumetric method as by the gravimetric. Accordingly the volumetric method would seem to recommend itself for use in ordinary routine work on

[1] Bureau of Animal Industry, U. S. Dept. of Agric.

account of its greater rapidity, simplicity, and probable equal ac-
curacy under ordinary conditions, while the gravimetric method may
be reserved for dips extremely high in rosin or for a confirmatory
method in special cases.

For the determination of rosin acids by either method it is most
advantageous to make use of the residue left in the distillation flask
after the estimation of phenols. From this residue all phenols
and a large part of the hydrocarbons have been removed, hence the
necessary extraction by ether is expedited. After cooling, the aque-
ous portion of the contents of the flask is poured into a separatory
funnel, with as little rosin as possible, and extracted with ether. The
aqueous portion is run off and discarded, the residue in the flask is
completely dissolved and brought into the funnel with ether, 40 to 50
c.c. of water is added, and the funnel well shaken. The presence of
insoluble carbonaceous matter will usually cause a persistent emulsion
at the junction of the 2 layers, which may, in fact, entirely fill the lower
part of the funnel.

This is wholly run off into a 300 c.c. Erlenmeyer flask and the
ethereal solution well shaken again with successive portions of water,
the water being run off each time to the clear ethereal solution, until
the carbonaceous matter is wholly removed and separation takes
place in the funnel quickly and cleanly. These wash-waters are all
received in the flask containing the first separated emulsion, and this
is heated upon the steam-bath until ether is expelled. The contents
are then brought more or less completely upon a wet filter and washed
with hot water. At this point the methods diverge.

Gravimetric Method.—In case the gravimetric method is to be
employed, after a brief washing of the insoluble carbonaceous residue
with hot water, both flask and filter are well drained. Both are then
washed, first with a little absolute alcohol to remove water, then thor-
oughly with ether until all rosin is dissolved and the filtrate comes
through colourless.

The united ethereal solution of hydrocarbons and rosin is now
thoroughly shaken with about 40 c.c. of 15% sodium hydroxide.
On separation there will be three layers. The lowest one usually
contains very little rosin soap, and consequently holds but a
small amount of hydrocarbons. It is best run off and washed
separately with ether. One washing will usually free it completely
from hydrocarbons.

After the first layer has been thus removed, about 50 c.c. of water is added to the funnel and the latter is well shaken. The lower layer of rosin soap is run off and followed by 5 to 10 c.c. of water without shaking, the funnel being given only a gentle rotatory motion. The remaining ether solution of hydrocarbons is washed twice with 20 to 25 c.c. of about 4% sodium hydroxide solution, each washing being followed by a little water as before described. These 2 washings with dilute sodium hydroxide are kept apart and not added to the main solution of rosin soap.

The main solution of rosin soap is now washed in a separatory funnel with successive portions of ether, followed through each time by 5 c.c. of water, as at first, until the ether is left nearly colourless. The ether extracts are shaken through in their order with the 2 washings of dilute caustic soda already used, and a third if needed, each being followed with a few c.c. of water.

All the aqueous extracts are united in a porcelain dish or casserole, which should be not more than half-filled by them, and are evaporated on the steam-bath until ether is dissipated and the volume reduced to a convenient amount. The contents of the dish are then transferred to a separatory funnel with the aid of a spatula and hot water; strong sulphuric acid is added to decompose all rosin soap, and after complete cooling the rosin acids are extracted by ether and washed with water till free from sulphuric acid. The ethereal solution is brought into a weighed Erlenmeyer flask with a few grains of sand, the ether is distilled off, and the flask is heated in an oven at 110° until the absence of frothing on rotation shows elimination of water; it is then cooled and weighed.

Volumetric Method.—As already noted, the volumetric method proceeds identically with the gravimetric to the point where carbonaceous matter is brought upon the filter and washed with hot water. The washing in this case must be continued until the wash-water comes through entirely free from acid reaction. The main ethereal solution has meanwhile been brought into a flask and the ether distilled off. The filter funnel is set in the neck of this flask, and the carbonaceous matter is washed with hot alcohol previously rendered neutral to phenolphthalein, until freed from rosin. The alcoholic solution of rosin is brought into a graduated flask, and an aliquot part, usually 1/4, taken for titration with N/2 sodium hydroxide. The titration is conveniently carried out in a 200 c.c. Erlenmeyer

flask in a volume of 100 to 125 c.c., the portion taken being diluted with neutralised alcohol to that amount.

Owing to the very dark colour of the liquid an external indicator is necessary. For this purpose alkali blue is best adapted. A few drops of a strong alcoholic stock solution are added to 25 or 30 c.c. of alcohol, which is then carefully neutralised with N/10 sodium hydroxide. Enough alkali blue should be added to produce a deep colour, almost a cherry, when neutralised, with no trace of violet. This dilute indicator should be freshly prepared. A supply of small test-tubes 8 to 10 mm. in diameter and 60 to 80 mm. long should be at hand, cleaned and dried. When a test of the progress of the titration is to be made about 1/2 c.c. of prepared indicator is poured into 1 of these test-tubes, and to this is added a drop of the liquid under titration. If a violet colour appears, the solution still contains free rosin acid, and more N/2 NaOH must be added and the solution again tested with a fresh tube of indicator. If the indicator does not show a violet colour upon the addition of 1 drop of the liquid under titration, addition of the latter is continued drop by drop until an amount has been added approximately equal in volume to the amount of indicator originally in the tube, i. e., 1/2 c.c. The continued absence of a violet colour after the addition of this amount indicates that the solution is either neutral or alkaline. The end of the titration then is reached when a greenish or violet tint just fails to appear. A fresh tube of indicator must be used for each test. It is best to proceed by running in 12 to 15 c.c. of N/2 sodium hyroxide at once, testing and continuing addition if necessary, a c.c. at a time, until the indicator shows alkalinity, then titrating back with N/2 hydrochloric acid, using perhaps 0.4 c.c. at a time till acidity is shown, and now working carefully with N/2 sodium hydroxide to exact neutrality. 1 c.c. of N/2 sodium hydroxide is considered to be equivalent to 0.162 grm. of rosin acids.

Phenolphthalein may also be used as an indicator in a similar way, by preparing an alcoholic solution of quite a deep rose tint. The end-point of the titration will then be reached when the indicator, used in the same way as alkali blue, is no longer bleached by the addition of the liquid under titration. The colour change is not so marked as in the case of alkali blue, and consequently the end-point is not so sharp, though almost equally good results may be obtained with a little care and practice.

All the alcoholic solutions should be kept from contact with air as far as possible to prevent absorption of carbon dioxide.

Determination of Occasional Ingredients.

Light oils.—The presence of light oils will usually be indicated by the relative proportions of oil and water which come over in the early stages of the process of distilling the dip for the estimation of water. The odour of the distillate should be noted at this point, to identify if possible the nature of the light oils present. If more information is desired, about 150 grm. of dip are thoroughly shaken with 20 to 25 c.c. of 1 : 3 sulphuric acid, allowed some hours to separate, and a weight of oils, etc., equivalent to 100 grm. of dip—*i. e.*, a weight in grm. equal to the sum of the percentages of hydrocarbons, phenols, and rosin—is distilled from an Engler flask fitted with a thermometer until the temperature reaches 180°. The distillate is measured and further examined in any way desired.

Naphthalene.—Too large a proportion of naphthalene or other solid hydrocarbons is undesirable on account of the liability of these bodies to separate from the dip in freezing weather and remain for a long time as an undissolved sediment. For an approximate estimation of the amount of solid hydrocarbons present 50 grm. of dip are acidified with a little concentrated hydrochloric acid, 100 c.c. alcohol added, and the containing vessel immersed in a freezing mixture for 2 hours, with occasional stirring. The separated hydrocarbons are then filtered off on a Buchner funnel or plate, washed somewhat with chilled alcohol, well drained, and pressed out in a letter-press between several thicknesses of filter-paper. The mass may then be weighed and subjected to any further examination desired. A more practical test is to subject a portion of the dip itself to a temperature of 0° for about 3 hours, with occasional shaking or stirring. It should remain perfectly clear and liquid and show no separation of solid matter.

Foreign Oils and Creosotes.—By the regulations of the Secretary of Agriculture (Bureau of Animal Industry Order 143, p. 18) the degree of dilution which may be accorded to a coal-tar creosote dip is explicitly made to depend upon the percentages of coal-tar oils and cresylic acid contained in the dip. Accordingly in the standardisation of dips for official use, within the scope of the regulations, petroleum oil,

rosin oil, or creosotes of other origin than coal-tar must be regarded as extraneous substances. Investigations are now in progress to find satisfactory methods for detecting and estimating these substances when present in dips. At the present time, however, this line of work has not reached a point of development which warrants the publication of any results.

CRESYLIC ACID DIPS.

Cresylic acid or cresol dips in composition approximate more or less closely the "liquor cresolis compositus" of the United States Pharmacopœia, eighth revision, 1905, being made from a potash-linseed oil soap and cresylic acid comparatively free from hydrocarbons. A properly prepared dip of this character should upon dilution in 100 parts of distilled water yield a practically water-clear solution, showing absence of any notable amount of hydrocarbons or unsaponified oil. On dilution, however, with hard water there will naturally be some turbidity, caused by the precipitation of soap. A portion of the dip when treated with successive small portions of water should show itself miscible in all proportions. At no stage should there be any notable turbidity of separation of heavy oily globules of cresylic acid due to absence of sufficient soap.

The methods of analysis adopted are essentially the same as for coal-tar creosote dips, modified in details to suit the somewhat different composition of the substances.

Estimation of Water.—The distillate must always be received in a stoppered cylinder and treated with benzol and sodium chloride solution as describ d. The results will be about 0.5% too low. The addition of toluene or a similar hydrocarbon to the dip before distillation might possibly improve the results.

Estimation of Potash (or Soda) and Pyridine.—A preliminary test is here necessary to determine whether potash or soda is the alkali present. The test may be conveniently made by shaking about 10 grm. of dip with ether and a little dilute hydrochloric acid, drawing off the aqueous layer, and applying the flame test with a platinum wire, supplementing this with any other confirmatory test necessary or desirable. If potash is found to be the alkali present the factor 0.471 must be used in place of the factor 0.31 employed in the case of soda.

Estimation of Phenols.—Since the percentage of phenols will here be much higher than in coal-tar creosote dips, a smaller amount of dip must be taken for analysis, usually 15 to 20 grm. The amount should be as large as possible, in order that the greatest quantity of phenols within the capacity of the tube may be brought to measurement. A new opportunity for error is here afforded. Linseed oil possesses a low Reichert-Meissl number, oo to 1.43 (See Vol. 2, page 70). This means that a small amount of volatile fatty acid will accompany the phenols through the stages of the process and tend to cause too high results. To determine the possible amount of this error 25 grm. of linseed oil was saponified, then acidified, and distilled with steam until 800 c.c. had been collected. The distillate was treated by the regular method and an increase in volume between 0.02 and 0.07 c.c. observed. In view of the fact that this quantity of soap is 4 or 5 times as much as would be present in an ordinary analysis, the error which is likely to arise from this source would appear negligible.

Estimation of Rosin or Fatty Acids.—The odour of the dip itself, and more especially the character of the residue left in the flask after the distillation of phenols, will inform the analyst whether rosin or fatty acids are to be determined. Rosin will collect in a solid, hard button at the bottom, while fatty acids will form a liquid oily layer floating upon the surface of the aqueous contents. In either case the whole is extracted with ether, washed with water, and, after evaporation of ether, dissolved in neutralized alcohol and titrated with $N/2$ sodium hydroxide. 1 c.c. of $N/2$ soda will represent 0.138 grm. fatty acid anhydrides (Lewkowitsch, J. Chemical Technology and Analysis of Oils, Fats, and Waxes, 3d ed., Vol. 1, p. 334, 1904) and 0.015344 grm. glycerin. Cresol dips containing rosin soap are not at present permitted in official dipping in the U. S. A.

Such a detailed analysis of a cresol dip would appear, however, seldom necessary. Phenols must of course be determined as accurately as possible. An examination of the odour and appearance of the residue left in the flask after distillation of phenols will indicate the character of the soap employed. If, then, the behaviour of the dip upon dilution is satisfactory and indicates the presence of sufficient soap, the only remaining question is whether there may be an unnecessary and possibly harmful amount of alkali present. In the presence of the large amount of cresylic acid contained in these dips there can be,

strictly speaking, no "free alkali." The ideal cresol dip will, however, unquestionably contain no alkali above that necessary to obtain complete saponification of the linseed oil. An excess of alkali can be of no possible benefit and might conceivably be undesirable for several reasons. A useful test for the presence of an excess of alkali is that of Kunofer (*Schweizerische Wochenschrift für Chemie und Pharmazie*, Jhrg. 46, No. 2, pp. 19–20. Zurich, Jan. 11, 1908).

10 grms. of dip are thoroughly shaken in a small separatory funnel with 30 c.c. of a saturated solution of NaCl. After complete separation has taken place the lower aqueous layer is removed, diluted with an equal volume of water, and a few drops of phenolphthalein added. If the dip has been made from a perfectly neutral linseed-oil soap, there will appear at most but a slight reddening of the solution, which vanishes upon the addition of a drop of $N/2$ acid. If more acid is required to remove the pink colour, the presence of an excess of alkali is indicated. The test cannot be made quantitative, for experiments have shown that only a part of the excess of alkali actually present is accounted for in this way, the remainder probably being thrown up in the form of alkali cresylate into the upper layer with the soap. It would seem, then, reasonable to demand that no dip treated as described should require more than a very few tenths of a cubic centimeter of half-normal acid to remove the pink colour imparted by phenolphthalein to the sodium chloride extract.

Duyk (*Ann. Chim. Anal.*, 1907, **12**, 345) proposes a method for the estimation of soap in cresol dips, according to which the soap is separated by shaking the dip with a strong sugar solution. The latter dissolves all the soap, which may be recovered by salting out with sodium chloride, and purified, if desired, by solution in alcohol.

PHENOLIC DISINFECTING LIQUIDS.

According to Engler and Dieckhoff (*Arch. Pharm.*, 1892, **230**, 562) cresol is only very slightly soluble in a solution of sodium acetate, but is miscible in all proportions with a 50% solution of sodium valerate. It also dissolves readily in a 15% solution of sodium oleate, 1 part of this compound rendering 5 parts of cresol soluble in water. Solution of rosin soap also dissolves cresols in large proportions. These facts explain the possibility of preparing phenolic disinfectant liquids

(*e. g.*, "creolin"), some of which contain as much as 50% of cresol acid. The aqueous solutions of the salicylates, benzoates, phenylacetates, etc., of the alkali metals, ammonia, and of aniline, also dissolve cresol, and their use for the preparation of soluble disinfectants containing the higher phenols has been patented by F. von Heyden (*Eng. Patent*, 1890, No. 9103).

While the higher phenols are rendered soluble in water by the presence of a suitable proportion of soap, the use of soap also furnishes a means of preparing aqueous solutions of hydrocarbons, the solubility of which is greatly increased by the simultaneous presence of phenols.

The popularity of phenol and the cresols as antiseptics and disinfectants has led to the production of many proprietary and patented preparations containing, or purporting to contain, these substances.[1] The following may be mentioned, but the sanitary applications of this class of bodies are of much less importance than formerly, since the more exact investigations of modern bacteriology have discredited in part the value of the phenols as germicides for internal use:

Creolin (Cresoline, Sanatol).—2 forms of this preparation are sold, known, respectively, as Artmann's and Pearson's. The former is obtained by the action of sulphuric acid on crude cresol. The latter contains cresol and some of the hydrocarbons of coal-tar held in solution by a resin-soap.

Lysol.—This is the fraction of coal-tar which boils between 190° and 200°, dissolved in fat and saponified. It is a clear, brown syrup, containing about 50% of cresols and is miscible with water. A little naphthalene is also present.

Saprol (which must not be confounded with *Asaprol*) is a mixture of crude cresols with some petroleum products.

Sapocarbol is a solution of crude cresols in a potassium soap.

Solutol and salveol contain sodium cresylate with excess of cresol.

The following method for the analysis of sheep dips and the foregoing phenolic disinfecting liquids is that employed in Allen's laboratory:

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[1] For a list and brief statement of the character of many of these preparations see *The Newer Remedies*, by V. Coblentz.

Treat 50 grm. of the sample with dilute sulphuric acid (1 : 3) until the liquid is distinctly acid to litmus, shake with ether, and separate.

Acid Liquid.	Ethereal Layer.		
Acid Liquid.—Render alkaline with sodium hydroxide and distil. Titrate distillate with N/2 acid, using methylorange as an indcator. (1 c.c. N acid neutralises 0.079 grm. *pyridine*.)	**Ethereal Layer.**—Shake with 20 c.c. (more or less, according to the amount of phenols, etc., supposed to be present) of a 25% solution of sodium hydroxide and separate.		
	Ethereal Layer.—Distil off ether and weigh residue of *hydrocarbons* (e. g., rosin oil, tar oil, naphthalene, etc.)	**Alkaline Liquid.**—Acidify with sulphuric acid (1 : 3) and distil until no more oily drops pass over.	
		Distillate.—Evaporate to low bulk with 20 c.c. of a 25% solution of sodium hydroxide (or sufficient to fix all the phenols), transfer to a burette, acidify slightly with sulphuric acid (1 : 3), keeping thoroughly cool all the time, and measure layer of *phenols*. The volume in c.c. multiplied by 1.05 equals the weight of phenols in sample taken.	**Residue in Retort.**—Shake with ether, separate, distil off ether and weigh residue of *fatty and resin acids*.

Ditz and Clauser (*Chem. Zeit.*, 1898, 732) have devised a process for the analysis of lysol, creolin, and similar preparations, depending on the fact that barium oleate is insoluble in water and but slightly soluble in 50% alcohol, whereas barium phenoxide dissolves in 40% of its weight of water at 100°, the orthocresoxide in 150%, the paracresoxide in 320%, while the rare metacresylate is very soluble. Barium oleate, however, being somewhat uncertain in composition, cannot be weighed as such; it is necessary again to liberate the oleic acid. Moreover, the fatty acids in lysol, etc., are not pure oleic, but contain stearic and palmitic as well, the barium salts of which are partially decomposed by water. Preliminary experiments have shown that with lysol, which usually contains about 40% of fatty acids and 40% of phenols, the amount of the former recovered is only 0.5% too low, and this is a deficiency of no importance in the present investigation. The operation is as follows: 5 grm. of the sample are dissolved in 100 c.c. of warm water, 20 to 30 c.c of 10% solution of sodium hydroxide added, and the mixture extracted 2 or 3 times with ether to remove the hydrocarbons. The ethereal solution is washed with very weak sodium hydroxide, and the latter combined with the bulk of the aqueous liquid; the ether is dried over solid potassium hydroxide, cautiously evaporated, and the residue dried over sulphuric acid to constant weight. The aqueous solution is carefully freed from ether on the water-bath, neutralised with hydrochloric acid, cooled completely (this is most important), and treated

with excess of barium chloride and a quantity of barium hydroxide solution roughly equivalent to the phenols present. The mixture is filtered quickly, avoiding unnecessary exposure to the air, the precipitate washed with barium hydroxide solution, then cold and finally hot water, rinsed back into the original beaker, decomposed with 1 : 1 hydrochloric acid, and thrown on to the first filter again. The oleic acid is washed with hot, weak acid till free from barium, with water till free from acid, dissolved in absolute alcohol and ether, and evaporated to constant weight at 100°.

The filtrate from the barium oleate, etc., may be acidified, extracted with ether, and the phenols recovered by evaporation; but it is better to operate as follows: In a convenient fraction of the acidified liquid the mixed phenols are determined by the Koppeschaar method (calling the bromine absorption calculated on the whole bulk x grm.). Another portion is extracted with ether, the solvent evaporated, and the residue dried for 2 or 3 hours at 100° to 110° (loss by volatilisation is of no consequence in this test). It is then dissolved in sodium hydroxide or barium hydroxide and titrated as before. The weight of the whole residue being a grm., its bromine absorption b grm., and the weight of the sample originally taken c grm., the percentage of phenols is given by the formula:

$$\frac{100 \, a \, x}{b \, c}$$

For the estimation of phenols in soap, Fresenius and Makin (*Zeit. anal. Chem.*, 1896, 325) recommend the decomposition of the soap by diluted sulphuric acid in slight excess, and distillation of the mixture in current of steam. The results are about 1% too high, owing probably to the presence of small amount of fatty acids in the distillate. The phenol in the distillate is determined by any suitable method.

W. Spalteholz (*Chem. Zeit.*, **22**, 1898) points out that in the examination of neutral substances, where the phenols are not in a state of combination, it is not necessary to add acid before distillation. The sample is placed in an iron retort and distilled in a current of steam between 200° and 220° until the distillate no longer yields any oily matter. Bodies which contain soaps of oleic acid must not be heated above 210° lest the latter are decomposed; this will be indicated by an oily layer on the top of the water in the receiver. Alkali-rosin soaps easily resist a temperature of 220°. The distillate consists of phenols alone in the case of lysol; of phenols and tar hydrocarbons in the case of

creolin, mixed with the water; and the simplest way of separating them is to extract the whole with benzene, remove the aqueous portion, and estimate the phenols themselves with sodium hydroxide.   With products of known composition the method has given results usually 0.5%, but occasionally 1.0%, below the theoretical, and it is therefore accurate enough for ordinary work.

DIHYDROXYBENZENES. DIHYDRIC PHENOLS.

The substitution of 2 hydrogen atoms in benzene by hydroxyl will give rise to 3 isomeric forms, exactly analogous in structure to the xylenols and cresols described in the preceding pages.
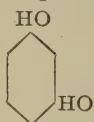
| Catechol, Pyrocatechin | Resorcinol, Resorcin | Hydroquinone, Quinol |
| (ortho-; 1–2) | (meta-; 1–3) | (para-; 1–4) |

All 3 forms are known.   They were originally obtained from natural products by destructive distillation, but are now mostly prepared by synthetic methods from benzene.   When the mono-halogenphenols (e. g., C_6H_4ClOH), phenolsulphonates, or benzene-disulphonates are fused with potassium hydroxide, the corresponding dihydroxybenzene is usually obtained, but the reaction is sometimes irregular, the meta-form being often produced when one of the isomerides is expected. The nature of the reactions is shown by the following equations:

$$C_6H_4I(OH) \quad + \; K(OH) = C_6H_4(OH)_2 + \; KI,$$
$$C_6H_4(OH)SO_3K + \; K(OH) = C_6H_4(OH)_2 + \; K_2SO_3,$$
$$C_6H_4(SO_3K)_2 \quad + 2K(OH) = C_6H_4(OH)_2 + 2K_2SO_3.$$
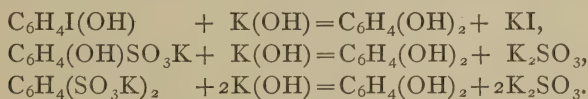
If the temperature be high, resorcinol is always obtained, as it is more stable than its isomers.   The 3 dihydroxybenzenes are volatile crystallisable bodies, readily soluble in water, alcohol, and ether, and extracted from their aqueous solutions by agitation with ether.   They form ethers when their hydrogen is displaced by alkyl-radicals, and resemble glycols in many respects.   The following table shows the chief distinctions between them.   In addition to the reactions given, resorcinol is characterised by its behaviour, with nitric acid, bromine, bleaching powder, and phthalic anhydride (see pages 337 and 338). Catechol and quinol exert marked reducing action at ordinary temperatures; resorcinol only at the b. p. of water.

	Catechol, Pyrocatechin Ortho- (1 : 2)	Resorcinol, Resorcin Meta- (1 : 3)	Quinol, Hydroquinone Para- (1 : 4)
Chief modes of formation.........	Fusion of phenol ortho-derivatives, kino, benzoin, or guaiacum, with caustic alkalies. Dry distillation of protocatechuic acid. Action of hydrogen iodide at 200° on guaiacol.	Fusion of phenol meta-derivatives, galbanum, asafœtida, etc., with caustic alkalies. Dry distillation of extract of brazil-wood. On the large scale from benzenedisulphonic acid.	Fusion of phenol para-derivatives with alkali hydroxides. Dry distillation of quinic acid. Hydrolysis of the glucoside arbutin, by dilute sulphuric acid. Reduction of quinone by aqueous sulphurous acid.
Appearance and crystalline form..	Rhombic prisms or thin pearly plates.	Rhombic prisms or plates.	Hexagonal prisms or monoclinic plates.
Sp. gr.............................	1.344	1.272	1.330
Action of heat....................	Melts at 104°; boils at 245°; may be sublimed, forming pungent fumes which excite coughing. Does not distil with steam.	Melts at 118°; boils at 276°; distils almost unchanged; volatilises with steam. Sublimes in silky needles.	Melts at 169°; sublimes when carefully heated, but decomposes if heated slowly.
Solubility........................	Very soluble in water, alcohol, and ether; extracted by ether from aqueous solutions.	Soluble in less than equal weight of cold water, very soluble in hot water; very soluble in alcohol, ether, and glycerol; extracted by ether from aqueous solutions. Nearly insoluble in chloroform, carbon disulphide, and cold benzene.	Soluble in 17 parts of cold water, very soluble in hot water. Very soluble in alcohol and ether; extracted by ether from aqueous solutions. Difficultly soluble in benzene.
Behaviour of aqueous solution with reagents:			
(a) Exposed to air in presence of alkali.	Becomes green, brown, and black.	Turns brown.	Turns brown.
(b) Colouration with ferric chloride (avoiding excess).	Dark green, changed to violet-red by ammonium hydroxide or acid sodium carbonate.	Dark violet, destroyed by ammonium hydroxide.	Forms green crystals of quinhydrone, changed to yellow, sparingly soluble quinone by excess of the reagent.
(c) Reaction with lead acetate..	White precipitate.	No precipitate.	No precipitate unless ammonium hydroxide be added.
(d) Reaction with silver nitrate.	Reduction of metallic silver in the cold.	No reaction in the cold; metallic silver reduced on boiling or on addition of ammonium hydroxide.	Metallic silver reduced on warming.
Taste of aqueous solution........	Bitter.	Sweetish.	Sweetish.

The *homologues* of the dihydroxybenzenes have as yet little importance. 6 dihydroxytoluenes are possible, of which the following four are best known:

CH₃   CH₃   CH₃   HO

HO   HO   HO   HO   HO   CH₃

           HO   HO   HO

Orcinol, Orcin   Homocatechol   Isorcinol   Toluhydroquinone
(1–3–5)   (1–3–4)   (1–2–4)   (1–4)
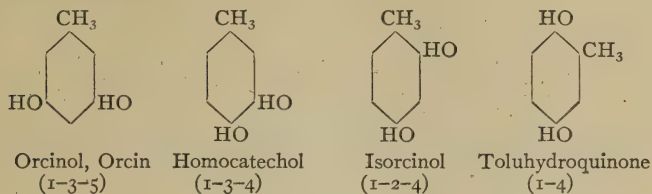
In toluhydroquinone the methyl group may be assumed to be at either 2, 3, 5, or 6, without changing the stereochemic relations. The methyl ether of homocatechol, $C_6H_3(OCH_3)(CH_3)(HO)$, is known as *creosol* (not to be confounded with cresol) and is found in beechwood tar (see page 350).

Resorcinol. Resorcin. Metadihydroxybenzene.

Resorcinol was originally obtained by the action of fused alkalies on certain resins, and subsequently by their action on metaiodophenol. It is now manufactured on a large scale by heating sodium hydroxide to about 250° with sodium metabenzenedisulphonate. The fused mass is allowed to cool, dissolved in water, and the solution acidified. From the solution, the resorcinol is extracted by agitation with amyl alcohol and purified by distillation under reduced pressure.

Resorcinol crystallises in rhombic prisms from water, alcohol, and ether, but in needles from benzene. The crystals gradually become pink, and appear phosphorescent when struck or rubbed in the dark. The odour is peculiar and the taste sweetish bitter. Fuming sulphuric acid dissolves resorcinol to an orange-red solution, which gradually darkens, becomes greenish-blue and then pure blue, and changes to purple-red on gently warming.

On adding bromine water to an aqueous solution of resorcinol, *tribromoresorcinol*, $C_6HBr_3(OH)_2$, is thrown down as a white flocculent precipitate consisting of crystalline needles, closely resembling tribromophenol. Resorcinol does not react with the usual indicators of neutrality, but with Poirrier's blue, C₄B, it behaves like a dibasic acid.

With hypochlorites resorcinol gives a violet, catechol an evanescent green, and quinol slowly develops a yellowish-red colouration.

When treated with excess of nitric acid, resorcinol is converted into a trinitroresorcinol, $C_6H(NO_2)_3(HO)_2$, 2:4:6. This body, formerly called styphnic or oxypicric acid, forms sulphur-yellow hexagonal crystals, melting at 175°. It closely resembles picric acid, except that it is astringent instead of bitter.

A solution of resorcinol, mixed with cupric sulphate and sufficient ammonium hydroxide to redissolve the precipitate first produced, yields a deep black liquid with which wool and silk may be dyed black.

Edlefson has observed that if a few drops of a 1% solution of resorcinol be added to a dilute, freshly-prepared, aqueous solution of β-naphthaquinone, and followed by a few drops of ammonium hydroxide, a dark bluish-green liquid is formed, from which ether does not extract the colour; but if sufficient nitric acid be added to produce an acid reaction, a red liquid is produced, from which the colour is extracted by ether or chloroform. Watson Smith (*J. Soc. Chem. Ind.*, 1886, 580) has confirmed these statements, and noted also that phenol, α-naphthol and β-naphthol do not give similar reactions.

When resorcinol is heated with excess of phthalic anhydride to about 200° for half an hour, the mixture acquires a yellowish-red colour, and contains the resorcinolphthalein or fluorescein, $C_{20}H_{12}O_5$. If the melt be dissolved in dilute sodium or ammonium hydroxide, the presence of resorcinol becomes apparent by the production of a dark red solution changing on dilution to reddish-yellow and yellow, and exhibiting after dilution a fine yellowish-green fluorescence, which is visible in solutions so weak as to appear colourless by transmitted light. On acidulating the solution and agitating with ether the fluorescein is taken up, and will be again dissolved on agitating the ethereal solution with soda. When similarly treated, *phloroglucinol* yields a yellow and *pyrogallol* a blue liquid, neither of which is fluorescent. The blue colour due to pyrogallol may be destroyed by cautious addition of potassium permanganate, which acts only slowly on the fluorescein. Catecholphthalein, formed by gently heating catechol with phthalic anhydride and a little sulphuric acid, dissolves in alkaline hydroxide solution with fine blue colour. Quinizarin, formed in a similar manner, dissolves in alkalies with violet-blue colour, and if the solution be acidified with sulphuric acid it becomes red, and the quinizarin may be extracted by agitation with ether and recovered from the ethereal solution by shaking with sodium hydroxide solution, which acquires a violet-blue colour.

Other properties and reactions of resorcinol are described on page 336.

When resorcinol is fused with excess of sodium hydroxide, phloroglucinol and some diresorcinol are produced.

Commercial resorcin usually contains from 92 to 94% of resorcinol, the remainder being chiefly phenol and tarry matters. A purer product is furnished for medicinal purposes. The solution in 10 parts of water should be colourless (empyreumatic impurities import a yellow tint), neutral to litmus, and should evolve no odour of phenol on warming. The solid should leave no residue on ignition.

According to the German Pharmacopœia, if 0.05 grm. of resorcinol be warmed with 0.1 grm. of tartaric acid in 10 drops of sulphuric acid, a dark carmine-red colouration is produced.

Resorcinol has marked antiseptic properties, and has been employed in medicine, but its chief value is derived from the numerous colouring matters obtainable from it.

Picrol is a trade-name for *potassium diiodoresorcinolmonosulphonate*, $C_6HI_2(SO_3H)(OH)_2$. It contains 52% of iodine, and is said to be powerfully antiseptic and not very poisonous.

Quinol. Hydroquinone. p-dihydroxybenzene, 1 : 3. (See also page 336).

Quinol may be prepared by the methods indicated on page 336, but is more conveniently obtained by oxidising aniline with chromic acid mixture and reducing the resultant quinone, $C_6H_4O_2$ with sulphurous acid.

Quinone, $C_6H_4O_2$, is a product of the oxidation of a great number of substances of the aromatic para-series. It is best prepared by dissolving 1 part of aniline in 8 parts of sulphuric acid and 30 parts of water, and adding 31.5 parts of powdered potassium dichromate. The liquid is allowed to stand for some time at the ordinary temperature, and is then warmed to about 35°. The quinone is extracted by ether or petroleum spirit.

Quinone crystallises with great facility from petroleum spirit in fine yellow needles or prisms which melt at 115.7°, but sublime readily at the ordinary temperature. Quinone has a peculiar, characteristic odour, and the vapour is very irritating both to eyes and nose, but the substance does not appear to be poisonous when taken internally. It dissolves moderately in cold water, very readily in boiling water and alcohol, and volatilises easily with steam.

Quinone liberates iodine from potassium iodide, and acts otherwise as an oxidising agent of moderate power. By sulphites, stannous chloride, and similar reducing agents it is converted into quinol.

Quinone can be estimated with accuracy, in the absence of other oxidising agents, by treating the solution with dilute hydrochloric acid and excess of potassium iodide, and titrating the liberated iodine by standard solution of sodium thiosulphate.

An extremely delicate reaction of quinone consists in adding to the dilute solution a few drops of a saturated solution of hydrocoerulignone, $C_{12}H_4(OCH_3)_4(OH)_2$. The liquid immediately acquires a yellowish-red colour, which rapidly becomes deeper, and steel-blue, iridescent needles of *coerulignone* separate out.

By the action of a mixture of hydrochloric acid and potassium chlorate, or of other powerful oxidising agents, quinone is converted into *tetrachlorquinone*, or *chloranil*, $C_6Cl_4O_2$. The same substance, mixed with *trichlorquinone*, $C_6HCl_3O_2$, is obtained by the action of hydrochloric acid and potassium chlorate on phenol, aniline, etc. Chloranil crystallises in golden-yellow plates or prisms, soluble in boiling benzene and moderately soluble in ether; but only slightly soluble in alcohol, and insoluble in water. Chloranil sublimes readily at about 200° and melts at a higher temperature. It is not attacked by strong sulphuric acid, nitric acid, or aqua regia. It is converted by reducing agents into colourless tetrachlorquinol. Chloranil is used in the colour-industry as an oxidising agent, as for converting dimethylaniline into chloranil violet.

Quinol has received a limited application in medicine. Its chief use is a developer in photography.

Catechol. Pyrocatechin. Orthodihydroxybenzene.

(See also page 336.)

Catechol is produced by the action of heat on protocatechuic acid, and on tannins and other bodies allied to it. It also results from the action of an excess of fusing potassium hydroxide on ortho-phenol-sulphonic acid, $C_6H_4(SO_3H)OH$.

Catechol is conveniently prepared from the fraction of beechwood-tar creosote boiling between 200° and 205°, which consists essentially of guaiacol or catechol methyl-ether. On heating this to the b. p., and passing in hydriodic acid gas as long as methyl iodide distils over,

catechol is produced and may be purified by fractional distillation and crystallisation from benzene. The reverse action is employed for producing guaiacol from catechol, which is now made on a considerable scale.

Catechol forms short, square prisms or thin, pearly plates, resembling benzoic acid. It sublimes readily and condenses in brilliant laminæ. The taste is bitter, and the fumes are pungent and excite coughing. Catechol differs from resorcinol in not volatilising appreciably in a current of steam.

The aqueous solution of catechol rapidly turns brown.

Catechol forms unstable compounds with bases. With lime-water an aqueous solution of catechol gives a reddish or brown colour, but the solution remains clear for some time. Alkali hydroxides behave similarly to lime-water, the solution becoming, in succession, green, brown, and black. Catechol is not precipitated by gelatin or alkaloids. With lead acetate it yields a white precipitate, which is easily soluble in acetic acid. Catechol reduces silver nitrate at ordinary temperatures and Fehling's solution on warming.

An aqueous solution of catechol gives no reaction with ferrous salts. With ferric chloride, avoiding excess, it gives a grass-green colouration, which on addition of acid sodium carbonate is changed to a fine violet-red, not much altered by boiling, but restored to green on the cautious addition of sodium hydroxide. (These reactions distinguish catechol from pyrogallol.) Pine-wood moistened with hydrochloric acid mixed with a solution of catechol acquires a violet-blue colour. Phloroglucinol gives a similar reaction.

The aqueous solution of catechol is neutral to litmus, but on addition of borax the liquid shows a marked acid reaction and acquires the power of decomposing carbonates. Pyrogallol and tannates and gallates of the alkali metals behave similarly. All these bodies belong to the ortho-series. Resorcinol, quinol, and orcinol, which contain hydroxyl-groups in the meta- or para-positions, do not form acid solutions on addition of borax.[1]

By treatment with sulphuric acid, catechol is converted into mono- or disulphonic acids, according to the temperature and the strength of acid employed (H. Cousin, *Comp. rend.*, **117** (1893), 113).

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[1] The thermo-chemical experiments of Berthelot and Werner have shown that, in case of polyphenols containing two hydroxyl groups in the ortho-position, one of these has an alcoholic and not a phenolic function, and this fact is related to the power of forming a conjugated acid with borax. (See *Comp. rend.*, **108** (1889), 1016, and *J. S. C.*, 1889, 845, 864.)

Homocatechol or Methylcatechol occurs as a methyl-ether in wood-tar creosote, and may be obtained therefrom by boiling with hydrobromic or hydriodic acid. Homocatechol is a syrupy liquid, which dissolves readily in water, alcohol and ether, but not in benzene (distinction from catechol). It reduces silver nitrate and Fehling's solution in the cold. With ferric chloride, homocatechol gives a green colouration, which is changed to reddish-violet on cautious addition of ammonia or sodium hydrogen carbonate.

By treatment with strong sulphuric acid, homocatechol yields a sulphonic acid. No disulphonic acid is obtainable.

Ethers of Catechol and Homocatechol.—By suitable means 1 or both the hydrogen atoms of the hydroxyl-groups of catechol and homocatechol can be replaced by alkyl-radicals. Thus, the following methyl ethers can be obtained:

Catechol.

$$C_6H_4 \begin{cases} OH \\ OH. \end{cases}$$

Methyl catecholate. Catechol methyl-ether. Guaiacol.

$$C_6H_4 \begin{cases} OCH_3 \\ OH. \end{cases}$$

Dimethyl catecholate. Catechol dimethyl-ether. Veratrol.

$$C_6H_4 \begin{cases} OCH_3 \\ OCH_3 \end{cases}$$

Homocatechol. Methylcatechol.

$$C_6H_3(CH_3) \begin{cases} OH \\ OH. \end{cases}$$

Methyl homocatecholate. Homocatechol methyl-ether. Creosol.

$$C_6H_3(CH_3) \begin{cases} OCH_3 \\ OH. \end{cases}$$

Dimethyl homocatecholate. Homocatechol dimethyl-ether.

$$C_6H_3(CH_3) \begin{cases} OCH_3 \\ OCH_3. \end{cases}$$

Guaiacol, creosol, and homocatechol dimethyl-ethers from the greater part of the fraction of beechwood-creosote boiling between 200° and 220° (see page 350). Veratrol is also very probably present. The dimethyl-ethers shown above can be prepared from guaiacol and creosol, respectively, by dissolving these bodies in a strong solution of potassium hydroxide in methyl alcohol and boiling with methyl iodide. They are distinguished from the monomethyl ethers by their insolubility in aqueous solutions of alkali hydroxides, and by giving no green or blue colouration with ferric chloride. Both the mono- and dimethyl ethers can be demethylated by heating them with excess of a halogen-acid, catechol and homocatechol being thereby formed.

Guaiacol. Methyl catecholate. Catechol methyl ether,
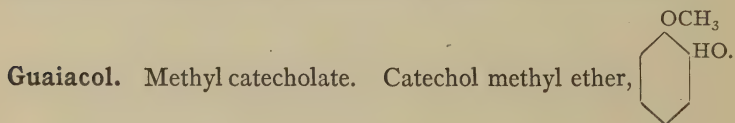
This substance has attracted much attention on account of its vogue as a remedy in tuberculosis. It is prepared from beechwood creosote by treating the fraction which distils between 200° and 205° with an alcoholic solution of potassium hydroxide by which potassium guaiacol is formed, and this is converted into guaiacol by the action of dilute acids. Guaiacol may also be prepared by several synthetic methods, as when catechol (1–2 dihydroxybenzene) is heated with equivalent quantities of postassium methyl sulphate and potassium hydroxide or sodium hydroxide. The action is:

$$C_6H_4(OH)_2 + K(CH_3)SO_4 + KOH = C_6H_4(OCH_3)(OH) + K_2SO_4 + H_2O.$$
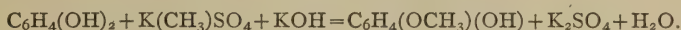
W. Kelle (Watson Smith, *J. Soc. Chem. Ind.*, 1898, 314) has devised a process for the production of guaiacol depending on the diazotising of 1–2 anisidine [methoxyaminobenzene, $C_6H_4(OCH_3)(NH_2)$] in the presence of excess of diluted sulphuric acid, after which the solution is run into a quantity of stronger sulphuric acid containing sodium sulphate, heated to 140°. The guaiacol is distilled as fast as formed by blowing steam through the liquid. The product is distilled at about 200° and the distillate crystallised on cooling. The reactions are:

OCH₃ / NH₂ (benzene ring) + NaNO₂ + 2H₂SO₄ = OCH₃ / N:NHSO₄ (benzene ring) + NaHSO₄ + 2H₂O

1–2-Anisidine. 1–2-Methoxydiazobenzene sulphuric acid.

OCH₃ / N:NHSO₄ (benzene ring) + H₂O = OCH₃ / OH (benzene ring) + H₂SO₄ + N₂
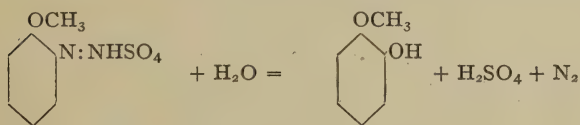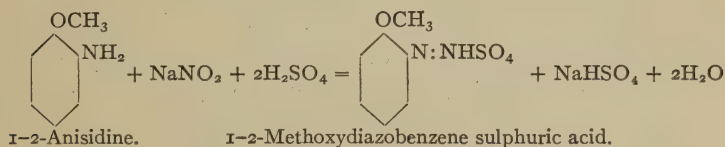
Pure guaiacol was formerly described as a liquid, but was obtained by Béhal and Choay (*Comp. rend.*, 116 (1893), 197) as a white solid, which, when crystallised from petroleum spirit, is obtained in hard, uniaxial, dihexagonal prisms. Guaiacol melts at temperatures variously stated at 28.5° to 33°, and boils at 204° to 205°. When melted, guaiacol remains indefinitely in a state of super-fusion, and may even be cooled to —2° without solidifying; but on addition of a crystal of the solid substance the whole immediately crystallises, the temperature ris-

ing to 27°. The sp. gr. of liquid guaiacol at 0° is 1.1543, and at 15° from 1.143 to 1.149. Guaiacol is only slightly soluble in water, but dissolves readily in most organic solvents, including absolute, but not aqueous, glycerol. It is also soluble in solutions of alkali hydroxides, and with an alcoholic solution of potassium (not sodium) hydroxide forms a crystalline mass of the potassium derivative. The same compound speedily separates on mixing equal measures of guaiacol and aqueous potassium hydroxide solution of 1.3 sp. gr. Impure guaiacol, even if containing 70% of the real compound, remains liquid under the same conditions. According to A. Trillat (*J. Soc. Chem. Ind.*, 1892, 1028) if 4 c.c. of guaiacol be shaken with 10 c.c. of milk of lime containing 0.1 grm. of lime, colourless crystals of a calcium derivative are formed.

Guaiacol has a sweet taste, and when placed on the tongue melts and produces a feeling of intense astringency, but it is without action on the mucous membrane.

According to P. Marfori, the physiological action of guaiacol is analogous to that of phenol or catechol, and it is eliminated from the system in a similar condition, but it is less poisonous than these bodies. Guaiacol has received an extensive application in medicine as a substitute for creosote in the treatment of phthisis, especially in the earlier states.

When treated in aqueous solution with ferric chloride, guaiacol gives a brownish turbidity; but if ferric chloride (avoiding excess) be added to a 1% solution of guaiacol in alcohol, a fine blue colouration is obtained, rapidly changing to green and yellow.

The following tests for guaiacol are given in the United States Pharmacopœia.

A colourless, crystalline solid, melting at 28.5° (83.3° F.), or a colourless, refractive liquid, boiling at 205° (401° F.), having an agreeable aromatic odour.

Sp. gr. of liquid, 1.140 at 25° (77° F.).

Soluble in 53 parts of water at 25° (77° F.), and in alcohol and ether in all proportions; soluble in acetic acid and in 1 part glycerin.

The addition of ferric chloride T. S., to an alcoholic solution of guaiacol (1 in 100) causes an immediate blue colour, changing to emerald-green, and finally becoming yellowish.

If 2 c.c. of guaiacol be shaken with 4 c.c. of petroleum benzin, the mixture should separate, on standing, into 2 distinct layers. Tur-

bidity or failure to separate into layers indicates the presence of impurities.

1 c.c. of guaiacol should dissolve in 2 c.c. of sodium hydroxide T. S., when heated, and, on cooling, the mixture should congeal to a white mass. Colouration or failure to congeal indicates the presence of impurities. The white mass thus obtained should form a clear solution with 20 volumes of water (turbidity indicates oily hydrocarbons).

1 c.c. of guaiacol, when added to 10 c.c. of concentrated sulphuric acid, should develop a pure yellowish colour in the liquid (a reddish colour indicating creosote).

The estimation of guaiacol is described under "Wood-creosote."

Commercial guaiacol is of very variable quality, some specimens being stated to contain not more than 30% of the pure substance, but good samples contain fully 90%. Inferior samples have a low sp. gr.—*e. g.*, 1.046—but those rich in guaiacol have a gravity approaching that of the pure substance. Pure guaiacol requires 8 times its measure of cold petroleum spirit for solution, but many commercial specimens are soluble in 4 measures or even less.

According to Marfori (*Gazzetta*, **20** (1890), 537), the solubility of guaiacol in water is notably reduced by the presence of impurities. Heated with chloroform and solid potassium hydroxide, pure guaiacol gives a purple-red colouration, while the impure product gives a less marked reaction. Marfori states that the pure substance gives with concentrated sulphuric acid a stable purple red colouration, while the least impurity detracts from the purity of the colour formed. On the other hand, some observers state that pure guaiacol gives no colour, or only a slight yellow, with cold strong sulphuric acid.

A number of compounds have been made synthetically for administering guaiacol so as to carry it unchanged through the stomach. Guaiacol carbonate is one of these compounds.

Guaiacol-carboxylic acid, $C_6H_3(OCH_3)(OH)COOH$, is obtained by saturating sodium-guaiacol with carbon dioxide under pressure, and decomposing the product with hydrochloric acid. It crystallises with $2H_2O$. The anhydrous substance melts at 148° to 150°, and decomposes into guaiacol and carbon dioxide at a higher temperature. It gives a blue colouration with ferric chloride.

Benzoyl-guaiacol, or *Guaiacyl Benzoate,* $C_6H_4(OCH_3)OCOC_6H_5$.—This compound, also called "*Benzosol*," is obtained by the reaction

of potassium-guaiacol and benzoyl chloride at 100°, or by the direct action of benzoic anhydride on guaiacol. It forms small colourless crystals melting at 50°, almost insoluble in water, sparingly soluble in glacial acetic acid, and readily soluble in hot alcohol, ether, or chloroform.

CREOSOL.

Homocatechol Methyl Ether,

$$
\begin{array}{c}
CH_3 \\
\bigcirc OME \\
OH
\end{array}
$$
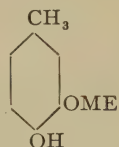
This substance is homologous with guaiacol, and occurs in the fraction of beechwood creosote boiling at about 220°. When freshly distilled, it is a colourless liquid, having a pleasant odour of vanilla, especially when dilute. It dissolves in aqueous alkalies, and with a strong solution of potassium hydroxide in alcohol sets to a mass of needles of the potassium compound, C_8H_9O. $OK + 2H_2O$. A solution of creosol yields a metallic mirror when warmed with silver nitrate, and gives a green colouration with ferric chloride. Creosol differs from guaiacol in its higher b. p. (219°), in not crystallising, and in its greater solubility in petroleum spirit. In its therapeutic effects creosol appears to present a close resemblance to guaiacol.

Creosol methyl ether, or *dimethyl homocatecholate*, $C_6H_3(CH_3):$ $(OCH_3)_2$, also occurs in beechwood creosote. It boils at 218°, gives no colouration with ferric chloride, and is insoluble in aqueous solutions of alkali hydroxides.

CREOSOTE AND CREOSOTE OILS.

The name "kreosot" was first applied by Reichenbach, in 1832, to the characteristic antiseptic principle contained in wood-tar (C. Rice, *Amer. Jour. Pharm.*, 1894, 167). Carbolic acid was discovered soon after by Runge in coal-tar, and was long confused with the wood-tar principle; and the crude carbolic acid from coal-tar is still known as "coal-tar creosote." Somewhat similar products are now obtained from other sources, so that much confusion has arisen. The term "creosote," when used without qualification, ought to be understood as signifying the product from wood-tar, but it is better to describe Reichenbach's substance as "wood-tar creosote," and employed the un-

qualified word "creosote" in a generic sense as meaning the mixed phenols and phenoloid bodies obtained from wood-tar, coal-tar, blast-furnace tar, shale-oil, bone-oil, or other sources. The term "creosote" should be restricted to the phenolic derivatives from the above or similar sources, the crude products from which they are derived being the corresponding "creosote oils." Some of these products differ materially in their chemical and physical characters, from the creosote from either wood- or coal-tar. These may be separated approximately from the accompanying neutral and basic oils by treating the fraction boiling between 170° and about 300° with potassium or sodium hydroxide, and then mixing the alkaline solution with a slight excess of dilute sulphuric acid, when the phenols are separated and form an oily layer of "creosote."

Wood-tar Creosote.

Wood-tar creosote is usually obtained by distilling beechwood tar, and treating the fraction heavier than water with diluted sodium hydroxide solution. The alkaline solution is separated from the insoluble oily layer, boiled with contact of air to oxidise some of the impurities, and decomposed by diluted sulphuric acid. The crude creosote which separates is purified by re-solution in alkali and re-precipitation with acid, and is then redistilled, the fraction passing over between 200° and 220° constituting purified creosote.

Virgil Coblentz (*J. Soc. Chem. Ind.*, **21,** 1431 (1902)) says that a good quality of beechwood creosote is not often met with upon the market. E. Gane is quoted to the effect that the majority of commercial wood creosotes consist either of low- or high-boiling products with very little or no guaiacol. Impure phenol (carbolic acid) is supplied under the misleading title "creosote" or "coal-tar creosote." In Massachusetts an analyst reported that 40% of the samples sold as creosote were impure phenol.

Wood-tar creosote is a strongly refracting liquid which is colourless when freshly distilled, but acquires a yellow or brown colour on keeping. It has a peculiar, persistent, smoky, aromatic odour, distinct from that of phenol. The sp. gr. ranges between 1.040 and 1.087. Wood creosote is not solidified by moderate cold. It is a powerful

antiseptic, but does not coagulate albumin. It preserves animal matters without causing disintegration as phenol is liable to do, and is less powerfully caustic than that substance.

Wood-tar creosote is only slightly soluble in water, but is with difficulty rendered anhydrous. Like absolute phenol and cresol, it is miscible in all proportions with alcohol, ether, glacial acetic acid, chloroform, benzene, and carbon disulphide. It dissolves in concentrated sulphuric acid to a red liquid, which slowly changes to purple-violet. Shaken with concentrated hydrochloric acid in the absence of air, wood-creosote becomes red, the colour changing in contact with air to dark brown or black. Wood-creosote is violently attacked by nitric acid. With bromine water it forms a derivative of a reddish colour.

Wood-creosote is soluble in solutions of caustic alkalies, and forms a crystalline compound with potassium hydroxide, but not with sodium hydroxide.

The United States Pharmacopœia furnished the following with respect to creosote.

Creosotum.—An almost colourless, yellowish (not pinkish), highly refractive, oily liquid, having a penetrating, smoky odour, and a burning, caustic taste; it should not become brown in colour on exposure to light.

Sp. gr. not below 1.072 at 25° (77° F.).

Its solution in about 140 parts of water at 25° (77° F.) is not perfectly clear. With 120 parts of hot water it forms a clear liquid, which, on cooling, becomes turbid from the separation of minute oily drops (distinction from, and absence of, both phenol and so-called "coal-tar creosote"). The filtrate from these separated oily globules yields a reddish-brown precipitate with bromine T. S. (distinction from phenol and so-called coal-tar creosote, both of which yield white precipitates). Soluble in all proportions in absolute alcohol, ether, chloroform, carbon disulphide, acetic acid, and fixed and volatile oils.

When distilled, most of it comes over between 200° and 220° (392° and 428° F.). When cooled to − 20°(−4° F.), it becomes gelatinous, but does not solidify (difference from phenol). It is inflammable, burning with a luminous, smoky flame.

Creosote is neutral or only faintly acid to litmus-paper.

On stirring together equal volumes of creosote and collodion in

a dry test-tube, no permanent coagulum should form (difference from phenol and so-called "coal-tar creosote," and limit of the former).

If 1 volume of creosote be mixed with 1 volume of 95% glycerin, a clear mixture will result, from which a creosotic layer, equal to or greater in volume than the creosote employed, will separate on the addition of 1/4 volume of water (difference from, and limit of, phenols).

On adding to 10 c.c. of a saturated aqueous solution of creosote 1 drop of ferric chloride T. S., the liquid develops a clear violet-blue colour, which is very transient; it then clouds almost instantly, the colour passing rapidly from a greyish-green into a muddy-brown, with finally the formation of a brown precipitate (difference from phenol and so-called "coal-tar creosote, and limit of the former).

If 1 c.c. of creosote be mixed with 10 c.c. of a solution of potassium hydroxide in absolute alcohol (1 in 5), a solid crystalline mass will form (difference from phenol and so-called "coal-tar creosote," and limit of the former).

On mixing 2 c.c. of creosote with 10 c.c. of normal sodium hydroxide V. S., a clear, pale yellow liquid results, which remains unclouded on cooling with 50 c.c. of water (absence of neutral oils).

If 1 c.c. of creosote be cautiously and gently shaken with 2 c.c. of petroleum benzin and 2 c.c. of freshly prepared barium hydroxide T. S. until a uniform mixture is produced, upon complete separation 3 distinct layers are visible, the middle one of which contains the creosote, unaltered in appearance; while the petroleum benzin should not be blue or muddy, and the aqueous layer should not have acquired a red tint (absence of coerulignol and some other high-boiling constituents of wood-tar).

Wood-tar creosote is a complex mixture of phenoloid bodies, the proportions of which differ according to the modes of distillation and purification. It may be regarded as composed of a mixture of bodies belonging to several homologous series, but chiefly of methylic ethers of catechol (pyrocatechol) and its homologues. *Asbolin*, a syrupy liquid, obtained by Braconnet from the soot formed by burning wood, has been shown by Béhal and Desoignes to be a complex mixture, containing catechol and homocatechol as leading constituents. Thus, the presence of the following bodies has been established:

Name	Formula	B. p. ,°
Monohydric Phenols		
Phenol..........................	$C_6H_5(OH$	182
Cresols (1–2, 1–3, 1–4).............	$C_6H_4(CH_3)OH$	203
Xylenols, phlorols (1–3–4, 1–3–5).......	$C_6H_3(CH_3)_2OH$	220
Ethyl-phenol (1–2)..................	$C_6H_4(C_2H_5)OH$	203
Ethers of Dihydric Phenols		
Guaiacol, methyl catecholate...........	$C_6H_4 \begin{cases} OCH_3 \\ OH \end{cases}$	200
Creosol, Methyl homocatecholate........	$C_6H_3(CH_3) \begin{cases} OCH_3 \\ OH \end{cases}$	219
Dimethyl homocatecholate............	$C_6H_3(CH_3)(OCH_3)_2$	214 to 218
Methyl creosol, dimethyl-guaiacol.......	$C_6H_2(CH_3)_2 \begin{cases} OCH_3 \\ OH \end{cases}$	above 230
Ethyl-guaiacol (1–3–4)...............	$C_6H_3C_2H_5 \begin{cases} OCH_3 \\ OH \end{cases}$	....
Propyl-guaiacol, cerulignol...........	$C_6H_3(C_3H_7) \begin{cases} OCH_3 \\ OH \end{cases}$	241
Ethers of Trihydric Phenols		
Dimethyl pyrogallate................	$C_6H_3 \begin{cases} OCH_3 \\ OCH_3 \\ OH \end{cases}$	253
Dimethyl methylpyrogallate...........	$C_6H_2(CH_3) \begin{cases} OCH_3 \\ OCH_3 \\ OH \end{cases}$	265
Dimethyl propylpyrogallate...........	$C_6H_2(C_3H_7) \begin{cases} OCH_3 \\ OCH_3 \\ OH \end{cases}$	285
Methyl propylpyrogallate............	$C_6H_2(C_3H_7) \begin{cases} OCH_3 \\ OH \\ OH \end{cases}$	290

Béhal and Choay (*Abst. J. Chem. Soc.*, 1894, 508) have reported the presence of a sulphur derivative, probably a thiophenol, in beech- and oak-tars; also a substance, distinct from pittacal, which, under the joint influence of ammonium hydroxide and air, yields a substance that produces with alkali an intense blue solution, changed to red on acidifying. Phenol is present in genuine wood-tar creosote in very small quantity, the cresols in somewhat larger, and the xylenols in sensible proportions; but the 2 chief constituents are guaiacol and

creosol. In Rhenish creosote, guaiacol predominates, but a sample of Morson's creosote from "Stockholm tar," examined by the author, boiled at about 217° and consisted chiefly of creosol. Dimethyl-guaiacol and propyl-guaiacol are present in but insignificant proportions, but the latter body is highly objectionable, since a single drop causes bleeding when placed on the tongue. Hence purified creosote should be absolutely free from this constituent, the presence of which may be recognised by the blue colouration produced with baryta-water.

The solubility of the constituents of creosote in alkalies decreases as the molecular weight increases, and with the number of hydroxyl groups substituted. Thus, methyl pyrogallate dissolves in a weak solution of sodium hydroxide, dimethyl pyrogallate, in a strong solution thereof, while trimethyl pyrogallate is insoluble in the cold alkali. Similarly, dimethyl homocatecholate, which constitutes the greater portion of the fraction of beechwood creosote distilling between 210° and 220°, is insoluble in aqueous solution of sodium hydroxide.

The following method may be employed for the separation of the phenoloid constituents of wood-creosote boiling between 195° and 240°, and might be used for the detection and estimation of coal-tar acids purposely added: The sample is dissolved in twice its measure of ether, and the solution shaken with a 5% solution of potassium hydroxide, which dissolves the phenolic substances. The alkaline liquid is separated, acidulated with hydrochloric acid, and shaken up with ether. The phenoloid oils obtained on evaporating the ethereal solution are distilled, mixed with half their volume of ether, and twice their volume of a saturated alcoholic solution of potassium hydroxide. Creosol and guaiacol are converted into crystalline potassium compounds, while the similar compounds of phenol and cresol remain in solution. The crystalline pulp is pressed through a cloth, the filrate evaporated, the residue treated with water, and the solution acidified with hydrochloric acid. The liberated phenols are re-treated with ether and alcoholic potassium hydroxide, the process being repeated, if necessary, so long as crystals are deposited in the cold, when the phenols are once more liberated, and may be weighed, measured, or titrated with bromine. The crystals may be dissolved in water and the solution decomposed by hydrochloric acid, when the guaiacol, creosol, and higher homologues are liberated, and may be purified and separated by fractional distillation. (Tiemann and Koppe, *Ber.*, 1881, 2005.)

The less volatile fractions of crude wood-tar creosote have been found by A. W. Hofmann to contain the methylic ethers of pyrogallol and its homologues. These bodies derive their chief interest from the remarkable colouring matters (originally discovered by Runge) which can be derived from them by oxidation. Thus, if the sodium dimethyl pyrogallate (prepared by adding sodium hydroxide to an alcoholic solution of dimethyl pyrogallate) be mixed with the sodium dimethyl methylpyrogallate and excess of sodium hydroxide, and heated in the air, a body called eupittonic acid is formed according to the following equation:

$$2C_8H_{10}O_3 + C_9H_{12}O_3 + O_3 = C_{25}H_{26}O_9 + 3H_2O.$$
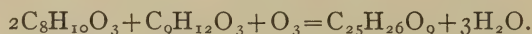
On oxidising the pyrogallic ethers from wood-tar creosote with more powerful reagents than atmospheric air, such as dilute chromic acid mixture, they are converted into quinones. Thus, dimethyl pyrogallate yields coerulignone, $C_{16}H_{16}O_6$, a substance which is identical with Reichenbach's "cedriret."

Beechwood oil is of very variable composition. The following results were obtained by Allen, in 1891, in the examination of 2 representative samples:

	No. 1	No. 2
Sp. gr.	1.0210	1.0130
Initial b. p.	110°	120°
Distillation commenced at	120°	140°
Distillate below 315°	66%	12%
Containing—		
Water	2%	1%
Phenoloids	40% } 40%	4% } 16%
Phenoloids in distillate above 315°	traces	12%

The phenoloids extracted from the oils by caustic alkali had the following characters, the whole 16% from No. 2 sample being mixed and examined together:

These results present a striking contrast. Even including the 12% in the portion of the oil distilling above 315°, No. 2 yielded only 16% of phenols. The large proportion of water taken up by the phenols of No. 2 is remarkable.

	No. 1	No. 2
Sp. gr.................................	1.0686	1.0760
Water..................................	7%	12%
Initial b. p.............................	103°	101°
Distillate below 220°....................	10 % (including 7% of water)	15% (including 12% of water)
Distillate below 230°....................	32%	25%
Distillate below 240°....................	52%	45%
Distillate below 250°....................	67%	50%
Distillate below 260°....................	76%	62%
Distillate below 270°....................	82%	....
Distillate below 280°ᐧ....................	86%	75%
Distillate below 290°....................	90%	76%

Béhal and Choay (*Compt. rend.*, **119** (1894), 166) give the following as the comparative composition of beechwood and oak creosotes, freed from hydrocarbons:

	Beech	Beech	Oak
Distillation temperature, °............	200 to 220	200 to 210	200 to 210
Sp. gr................................	1.085	1.085	1.068
Monophenols..........................	39.0	39.0	55
Guaiacol..............................	19.7	26.5	14
Creosols and homologues..............	40.0	32.1	31
Loss..................................	1.3	2.4	....

In making the foregoing analyses, the heavy oil was acidified with hydrochloric acid and agitated with water to remove certain basic substances. The oily layer was then treated with sodium hydroxide, a very considerable quantity of water added (since concentrated alkali solutions of phenols dissolve a certain quantity of indifferent oils), the undissolved oil separated, the alkaline liquid shaken with benzene to remove traces of hydrocarbons, etc., and then treated with a current of steam until the distillate no longer smelled strongly. The phenols were then set free by hydrochloric acid, separated, the acid liquid agitated with benzene, and the phenols thus extracted recovered by evaporating off the benzene and added to the main quantity.

From these results it would appear that the fraction of beechwood creosote distilling between 210° and 220° contains no guaiacol. Oak creosote contains less guaiacol and more monophenols than the beech-

wood product, and it is to the presence of these latter constituents that
oak creosote owes its greater causticity.

The following figures shows the results obtained by Allen, in 1891,
by the examination of 4 typical samples of beechwood creosote as
supplied by leading manufacturers:

	A	B	C	D
Initial b. p...................	....	....	201°	198°
First drop distilled at..........	197°	218°	210°	204°
Distillate below 207°..........	....	....	....	10%
Distillate below 209°..........	....	....	....	25%
Distillate below 210°..........	5%	....	....	48%
Distillate below 213°..........	....	....	....	65%
Distillate below 215°..........	20%	....	10%	78%
Distillate below 216°..........	....	....	25%	....
Distillate below 217°..........	35%	....	28%	82%
Distillate below 218°..........	42%	....	45%	....
Distillate below 219°..........	50%	....	50%	92%
Distillate below 220°..........	53%	5%	60%	....
Distillate below 221°..........	....	....	64%	95%
Distillate below 222°..........	....	....	70%	....
Distillate below 223°..........	63%	28%	....	....
Distillate below 224°..........	....	....	82%	....
Distillate below 225°..........	70%	50%	....	....
Distillate below 226°..........	....	....	90%	....
Distillate below 227°..........	77%	64%	....	....
Distillate below 228°..........	....	....	95%	....
Distillate below 230°..........	84%	78%	....	....
Distillate below 235°..........	90%	90%	....	....
Sp. gr......................	....	....	1.0656	1.0778
Behaviour with baryta water...	Distinct reaction	No reaction	No reaction	Slight pink colouration
Behaviour with alcoholic potash.	Solidified	....	Solidified at once	Solidified on standing

These results indicate almost entire absence of guaiacol from A,
B, and C, and almost entire absence of creosol also in the case of B.

A detailed analysis of beechwood creosote distilling between 200°
and 210° is given by Béhal and Choay as follows:

Phenol..	5.2
1–2-cresol..	10.4
1–3- and 1–4-cresols	11.6
1–2-ethylphenol...	3.6
1–3–4-xylenol..	2.0
1–3–5-xylenol..	1.0
Phenols, various...	6.2
Guaiacol..	25.0
Creosol and its homologues..................................	35.0
	100.0

According to this analysis, the proportion of guaiacol in beechwood
creosote is much smaller than is usually stated. Allen's results

(already given) obtained by distilling commercial creosote go generally to confirm the above figures, but show that the composition of the product is very variable. Fréyss states that commercial beechwood creosote contains from 3 to 30% of guaiacol, from 10 to 40% of creosol, and a very variable proportion of monophenols.

Phenol is detected, according to M. E. Merklen (*Zeits. Anal. Chem.*, 1901, **40**, 621–3), as follows: 4 c.c. of creosote are heated with 1 c.c. of ammonia to 60°. The mixture is spread over the surface of a large basin and subjected to the action of bromine vapour. If phenol is present, a blue colouration is obtained. Pure creosote gives a brown or green colour.

In consequence of the large demand of recent years for guaiacol and its preparations, much of the wood-creosote now sold has been deprived of its guaiacol, so that it is now rare to find specimens containing even 20% of that constituent.

Quantitative Wood-creosote.

Béhal and Choay (*Comp. rend.*, **116** (1893), 197) have devised a method for the estimation of guaiacol in wood-creosote, based on the following principles: 1. Treatment of the sample with hydrobromic acid, whereby the methyl ethers of the polyphenols are completely demethylated. Thus, guaiacol by such treatment yields catechol, and creosol gives homo- or methyl-catechol. 2. Distillation of the demethylated oil in a current of steam, whereby the monophenols (phenol, cresols, xylenols) are carried over and are thus separated from the polyphenols. 3. Extraction of catechol, homocatechol, and any traces of unvolatilised monophenols by ether. 4. Separation of catechol from homocatechol by treatment with benzene, which dissolves the former substance only. The following are the working details of the process as modified by M. Adrian (*Nouv. Rem.*, **13**, 97; Abst. *J. Soc. Chem. Ind.*, 1897, 367): 100 grm. weight of guaiacol or creosote are placed in a flask of 250 c.c. capacity, connected on the one hand with another flask which serves as a generator of gaseous hydrogen bromide (generated by the action of water on phosphorus tribromide) and on the other with an inclined reflux condenser. The exit-tube from the condenser leads the gas through 2 wash-bottles containing water. The delivery tube between the generator and the guaiacol is furnished with a large bulb to prevent aspiration of the

liquid when cooling. The gas is allowed to pass slowly through the guaiacol, which is gently warmed after the process has been in operation for half an hour, and continued for 90 minutes. It is then cooled, transferred to a large flask, diluted with 5 or 6 volumes of water, and all volatile bodies removed by steam distillation. When no more oily liquid comes over, the distillation is stopped, the catechol in the residual liquor extracted, together with homocatechol, by washing out with ether, the ether cautiously distilled off, and the residue dried. This is then treated with dry benzene, which extracts the whole of the catechol produced by demethylation of the guaiacol originally present, leaving the homocatechol undissolved. From the solution of benzene the catechol is crystallised out and weighed. Care must be taken at the end of the process to avoid the least trace of moisture in the residue and in the solvent, or crystallisation will not take place; and even with perfectly dry benzene the mother-liquor must be concentrated and the catechol which crystallises out added to the main quantity.

The monophenols which distil with steam are separated by Béhal and Choay by fractionation and subsequent conversion into benzoates The methyl derivatives of the diphenols are separated by precipitation with strontium hydroxide, the precipitate being decomposed by hydrochloric acid. They are then fractionated, and, if necessary, converted into carbonates by carbon oxychloride, and further separated by fractional crystallisation.

L. F. Kebler (*Amer. Jour. Pharm.*, 1899, 409) has described the following process of estimating guaiacol in creosote: 5 c.c. of the sample are mixed with 50 c.c. of a 20% solution of potassium hydroxide in alcohol. The crystalline mass of the potassium derivatives of guaiacol and creosol, which forms in the course of 1/2 hour, is pressed between filter-paper until dry and treated in a test-tube with 5 c.c. of 20% sulphuric acid. On heating the mixture, the guaiacol and creosol rise to the surface. The liquid is then diluted with sufficient water to cause the oily layer to sink, when the aqueous portion is decanted and the oil treated with 4 c.c. of concentrated ammonium hydroxide. A hard crystalline compound is immediately formed by the guaiacol, and a semi-crystalline mass is given after some time by the creosol. On treating the crystalline mixture with petroleum spirit, all but the ammonium compound of guaiacol is dissolved, and this can be purified by filtration and washing with petroleum spirit.

The compound is then decomposed by dilute sulphuric acid, the liberated guaiacol extracted by agitation with petroleum spirit, and the solution evaporated in a tared flask.

Kebler finds the proportion of guaiacol in commercial wood creosote to range from 16% down to *nil*, and doubts the statement that creosote ever contained 60% of guaiacol. He suggests that a range of b. p. from 200° to 220° should be permitted. This extension would admit creosol to an equality with guaiacol as a legitimate and valuable constituent of creosote, which would appear to be justifiable both from analogy and from what is positively known of the therapeutic action of creosol.

Kebler gives the following data obtained by the examination of six samples of commercial wood-creosote, purchased in the United States, though the results show that none of the samples complies with the requirements of the United States Pharmacopœia:

	1	2	3	4	5	6
Sp. gr.	1.0748	1.0748	1.0650	1.0642	1.049	1.069
Percentage distilling below 200°	5	20	None	None	18	32
Percentage distilling from 200° to 205°	34	20	None	None	12	18
Percentage distilling from 205° to 210°	26	30	None	2	12	8
Percentage distilling from 210° to 215°	23	19	30	37	39	24
Percentage distilling from 215° to 220°	6	7	25	21	14	9
Percentage distilling from 220° to 238°	3	1	40	36	....	4
Behaviour with diluted glycerol	Normal	Normal	Emulsion	Emulsion	Emulsion	Normal
Number of c.c. of 7 1/2% NaOH required to dissolve 2 c.c. of sample	9	·8	9	7	8	8
Behaviour of 1 c.c. of sample when mixed with 20 c.c. of a 20% solution of KOH in absolute alcohol	Crystals in 15 minutes; solid in 40	No crystals in 5 hours; solid in 18 hours	Crystals in 4 minutes; solid in 15	Solidified almost immediately.	Solidified on cooling	Solidified on cooling
Percentage of guaiacol..	None	None	8	16	....	......
Percentage of mixed potassium compounds of guaiacol and creosol (page 356)	60	48	60	106	....	......

A useful indication of the proportion of guaiacol present in wood-creosote is afforded by the sp. gr. of the sample, or preferably of the fraction distilling between 200° and 205°. The specimens having the highest sp. gr. are richest in guaiacol. The United States Pharmaco-

pœia (1900) requires wood creosote to have a sp. gr. not below 1.072 at 25°. The British Pharmacopœia (1898) is slightly more rigid, requiring a sp. gr. of not less than 1.079.

Creosote is commonly stated to be optically active. The British Pharmacopœia of 1885 alleged that it was dextro-rotatory, while the edition of 1898 asserts that it is levo-rotatory, both statements being misleading. As a rule, wood creosote exhibits no sensible optical activity, and the same is true of pure guaiacol and creosol. Occasionally, specimens of creosote are met with which exhibit an insignificant activity, but the character is valueless as a practical test.

Wood-tar creosote of good quality has an agreeable, vanilla-like odour, and darkens in a marked manner on prolonged exposure to light.

An alcoholic solution of wood-tar creosote should not give any colouration whatever (neither blue nor reddish) with barium hydroxide. The test may be made by dissolving the creosote in twice its volume (or a sufficiency) of petroleum spirit, which should form a perfectly clear solution; and on shaking this liquid with an equal volume of saturated baryta water no blue, violet, or red colour should appear in either stratum. Such colours indicate the presence of *coerulignol* or other objectionable impurities.

Wood-tar creosote is practically insoluble in strong solution of ammonium hydroxide, and when shaken with 1 or 2 volumes thereof (sp. gr. 0.880) the mixture separates on standing into 2 layers, of which the lower or creosotic layer considerably exceeds the volume of the sample used.[1] Genuine and pure wood creosote, when agitated with ammonium hydroxide, will not acquire a colour deeper than lemon-yellow in half an hour, and the upper aqueous stratum should be pale or yellowish. In 24 hours the creosote should have acquired a brown or olive-green tint—not blue.

Adulterations of Wood Creosote.—Wood-tar creosote has been sometimes adulterated with, or wholly substituted by, the crude phenols of coal-tar. The reactions of the cresols and xylenols resemble those of wood creosote still more closely than do those of phenol, and many of the proposed tests for differentiation are valueless.

The reactions described below have been carefully studied by

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[1] According to the British Pharmacopœia (1898), if wood creosote be agitated with five times its measure of solution of ammonium hydroxide (sp. gr. 0.959) its volume will not be diminished materially unless coal-tar phenols be present.

Allen on specimens or pure phenol, Calvert's No. 5 carbolic acid (representing cresols), and Morson's creosote. The descriptions should be compared with the reactions of phenol and cresol given on page 316.

a. Wood-tar creosote is also distinguished from the coal-tar acids by its reaction with an ethereal solution of nitrocellulose. Shaken with half its volume of collodion, Calvert's No. 5 carbolic acid coagulates the guncotton to a transparent jelly, best observed by inclining the tube and causing the liquid to flow gently from one end to the other. Morson's creosote does not precipitate the nitrocellulose from collodion, but mixes perfectly with the ethereal solution. Addition of much wood creosote to a mixture of collodion and a coal-tar acid causes a re-solution of the precipitated nitrocellulose. When a mixture of equal volumes of Morson's creosote and Calvert's No. 5 carbolic acid is shaken with half its volume of collodion, decided signs of precipitation are observed. With 2/3 of the coal-tar acids to 1/3 of creosote, the precipitation of nitrocellulose is very marked.

b. When carefully used, a solution of ferric chloride affords a very satisfactory means of distinguishing wood creosote from coal-tar acids, but not for distinguishing either in mixtures of the two. The reaction produced varies, however, in a somewhat curious manner, according to the way in which the test is performed, the following being, in the author's experience, the most satisfactory methods of operating: 1. On placing a drop of Morson's wood-tar creosote in a hemispherical porcelain dish and adding a few drops of neutral solution of ferric chloride, a yellowish-brown colouration is produced, and on stirring the undissolved creosote acquires a reddish-brown and the ferric solution an olive-brown tint. Calvert's No. 5 carbolic acid, when similarly treated, acquires a light straw-colour, while the ferric solution assumes a fine violet colouration, which is permanent. On slightly diluting the mixtures with alcohol they both yield olive-brown solutions, but on further addition of alcohol the creosotic mixture becomes a light olive-brown tint with a shade of green, while the carbolic solution turns light brown or amber without any green tinge. 2. On the other hand, if a drop of wood creosote be dissolved in 10 drops of alcohol, and a drop or two of dilute ferric chloride added, a bluish-green colouration is produced, changing to a fine green, while Calvert's No. 5 carbolic acid yields a greenish-blue colour under simi-

lar conditions.   On adding sufficient ferric chloride to precipitate the
wood creosote from its solution, an olive-brown colouration changing
to deep brown is obtained; while the carbolic mixture retains its green-
ish-blue tint, though more or less disguised by the yellow colour of the
ferric solution.   3. The addition of 1 drop of a 10% aqueous solution
of ferric chloride to 15 c.c. of an aqueous solution of wood creosote
produces a green colouration, changing very rapidly to brownish-yellow.
The solution of a coal-tar acid when similarly treated gives a perma-
nent violet-blue colouration.

c. Morson's wood-tar creosote is sharply distinguished from the
coal-tar acids by its insolubility in absolute glycerol (sp. gr. 1.258),
whether 1, 2, or 3 times its volume of the liquid be employed.   Other
varieties of wood creosote are somewhat more soluble in glycerol,
but the solutions are readily precipitated on adding water.   Guaiacol
dissolves in absolute glycerol, but is precipitated by dilution.

d. Hager modifies this test by using somewhat diluted glycerol.
3 measures of absolute glycerol mixed with 1 volume of water
in an appropriate strength.   For the detection of coal-tar acids in
wood creosote, 1 volume of the sample should be thoroughly agitated
in a Mohr's burette with 3 volumes of the diluted glycerol, and the
liquid allowed to stand till separation has occurred.   If the creosote
be pure, the volume will remain unchanged.   If reduced, the glycerol
layer is tapped off, and the remaining creosote again shaken with
3 times its volume of diluted glycerol and the volume again observed.
This second treatment will always suffice for the removal of the coal-
tar acids, unless their proportion is very large, and hence the volume
of the residual layer will indicate the proportion of real wood creosote
in the quantity of the sample taken.   The nature of the residual
creosote can be verified by the collodion test (*a*), while the coal-tar
acids can be recovered from the glycerol solution by filtering it to
remove suspended traces of wood creosote, diluting with water, and
agitating with chloroform.   On spontaneous evaporation of the sepa-
rated chloroform, the coal-tar acids are obtained in a condition of
sufficient purity to allow of their positive recognition.

Hager's modification of the glycerol test for creosote was examined
in Allen's laboratory by W. Chattaway with fairly favourable results.
The following figures, obtained with mixtures of wood creosote and
Calvert's No. 5 carbolic acid, show the approximation to the truth of
which the method is capable:

Taken		Found	
Wood creosote	Coal-tar phenols	Residual layer	Recovered by chloroform
9 c.c.	1 c.c.	9.0 c.c.	0.96 grm.
8 c.c..	2 c.c.	8.0 c.c.	1.82 grm.
6 c.c.	4 c.c.	6.3 c.c.	3.46 grm.
4 c.c.	6 c.c.	4.0 c.c.	5.22 grm.

The portion left undissolved after the second treatment with dilute glycerol had all the characters of wood creosote. It did not coagulate collodion. The portion dissolved by the glycerol and subsequently recovered by chloroform behaved like coal-tar acids with collodion and ferric chloride. Hence the separation by glycerol is fairly perfect.

From the foregoing reactions it will be seen that phenol, cresols, and wood-tar creosote can be readily distinguished from each other. The case is different when a mixture of the substances has to be dealt with, as in the case of a sample of wood creosote adulterated with crude carbolic acid. As the problem is to detect the coal-tar acids in presence of wood-tar creosote, rather than the reverse, only affirmative tests for the former bodies are of service, and in many cases these are seriously modified by the simultaneous presence of creosote. In fact, the reactions with glycerol and collodion are the only 2 simple tests of real service, and these are much affected by the presence of a considerable proportion of wood creosote. If, however, the sample be treated with diluted glycerol, as described under *d*, and the ferric chloride and collodion tests be applied to the residue recovered by chloroform from the glycerol solution, the recognition of the coal-tar acids can be satisfactorily effected. These tests are best applied to the portion dissolved by the first treatment with glycerol, a second treatment being necessary to complete the extraction of the coal-tar acids, but the additional quantity dissolved is liable to contain sufficient creosote to obscure the blue colouration with ferric chloride. In employing these tests it must be remembered that genuine wood-tar creosote contains distinct traces of phenol and cresols and still more of xylenols, and hence adulteration should not be assumed unless the treatment with diluted glycerol effects the removal of a very notable quantity of coal-tar acids.

A possible addition to wood-tar creosote, but one which does not appear to have been noted, is that of *blast-furnace creosote*. This, being of very similar composition to wood creosote, is very difficult to detect. The phenolic substances from blast-furnace creosote oils were distilled, and the fraction passing over between 210° and 220° examined in Allen's laboratory by the foregoing tests for wood creosote. The fraction itself readily gelatinised collodion, and gave with ferric chloride (test *b* 1) a slate-blue colouration changing to dirty brown. On treatment with diluted glycerol the greater part remained undissolved, but the dissolved portion when recovered by chloroform had the odour of common phenol, coagulated collodion, and reacted with ferric chloride almost exactly like Calvert's No. 5 carbolic acid, except that by test *b* 1 the violet-blue changed to brown instead of being permanent. These reactions would allow of the detection of blast-furnace creosote in wood creosote, but the insolubility of the greater part of the former product in diluted glycerol would render a separation of the two impossible by that means. If the adulteration of wood creosote by the portion of the blast-furnace product insoluble in glycerol were to be attempted, the reaction with ferric chloride and the gelatinisation of collodion would suffice to detect the substitution. The same is true of the fraction boiling below 240° of the *phenoloid* bodies from a crude *shale oil*, in addition to which their peculiar odour would attract attention.

Blast-Furnace Tar Creosote.

The tar obtained by cooling the waste gases from blast furnaces (see page 18) yields very little naphtha on distillation, and hence the "creosote oil" consists of the whole distillate up to the point at which the oils solidify on cooling. Blast-furnace creosote oil is a thin, brown liquid, lighter than water. It contains no naphthalene, but is rich in basic constituents and phenols.

On treating 14 gallons of creosote oil (sp. gr. 0.988) condensed from blast-furnace gases with sodium hydroxide solution of 1.07 sp. gr. (6% NaOH), and decomposing the solution with dilute sulphuric acid, Watson Smith (*J. Soc. Chem. Ind.*, 1883, 497) obtained 2 gallons of crude creosote as a dark brown liquid of 1.07 sp. gr. On fractionally distilling this product Smith obtained only 1.33% of phenol boiling at 182°, whereas the tar acids from Lancashire coal-tars yield about

65% of crystallisable phenol. The fraction which would contain the cresols amounted to 4.5% of the total tar acids. The larger fraction (19.4%) distilling between 210° and 230°, probably consisted mainly of xylenols with guaiacol and creosol. These results show that a close similarity exists between the phenolic substances of blast-furnace creosote and those contained in wood-tar. A large proportion of the creosote distilled at a temperature above 230°, but the exact nature of this fraction is not at present known. The fraction distilling above 360° gave, on treatment with sodium hydroxide and exposure to air, unstable colouring-matters, which are probably allied to the eupittonic acid obtained from wood-tar.

It is probable that the extraction of the phenolic substances from the sample examined by Smith was not complete, as he used a dilute alkali. By repeatedly treating a sample of blast-furnace creosote oil of 0.956 sp. gr. with 19% solution of sodium hydroxide (sp. gr. 1.21), Allen extracted 34% by volume of tar acids, having a sp. gr. of 1.0355. 100 c.c. of these acids gave very little distillate below 200° and 59.5% below 250°, the largest fraction (24%) distilling between 220° and 230°. The fraction distilling between 210° and 220° is described on page 347. On treating a portion of the mixed tar acids extracted by strong alkali with dilute sodium hydroxide solution (3.5% of NaOH), separating the insoluble portion, and acidifying the aqueous liquid, the phenols obtained were completely soluble in dilute glycerol, and gave a fine violet-blue colouration with ferric chloride.

In a later contribution (*J. Chem. Soc.*, **49** (1886), 17), Smith reports the detection of the following constituents of blast-furnace creosote: Ordinary phenols, cresols (chiefly 1–3), xylenols (chiefly 1–3–4), trimethylphenols, and naphthols.

2 samples of the blast-furnace creosote oil examined by L. Archbutt had a sp. gr. of 0.969 and 0.956, respectively, and yielded 35 and 29% of phenols to sodium hydroxide solution of 1.21 sp. gr. (19% NaOH).

The phenol of blast-furnace tar contained in the "neosote" of commerce are chiefly cresols.

Neosote.—The phenol of blast-furnace tar (page 18) have been patented by Allen and Angus under the name of *neosote* ("new preservative"). This is obtained by treating blast-furnace creosote oil with sodium hydroxide, separating the insoluble hydrocarbon oils, and

decomposing the solution of the sodium compound by the waste gases from the blast furnaces. The carbon dioxide in the gases converts the sodium into carbonate and the phenols are set free. The solution of sodium carbonate is causticised with lime, and thus furnishes sodium hydroxide for treating a fresh quantity of the creosote oil. The crude phenols are redistilled, the distillate constituting the "neosote" of commerce. The figures in the table obtained by Allen show the behaviour of a typical sample of neosote when distilled with a Glynsky's fractionator.

It will be observed that 27.8% passed over between 195° and 200°, and an additional 19.8% between 200° and 205°. The temperature remained absolutely constant at 197° for a considerable time, and again at 204°. The regular decrease in the sp. gr. of the fractions is interesting. The original sample contained 3.15% of hydrocarbons.

Neosote contains only 1 or 2 units % of crystallisable phenol, a large proportion of cresols, and gradually decreasing proportions of the higher homologues. Oxyphenols, similar to or identical with those of wood creosote, are also present, but the method of purification adopted eliminates a large proportion of these constituents. When freshly distilled, neosote is almost as colourless as water, but it acquires a dark yellow or brown colour by keeping. Experiments made to test the antiseptic value of neosote have shown that it is fully able to compare with crude carbolic acid, while its caustic properties (when applied in a concentrated condition to the skin) appear to be much less marked than those of the gas-tar product.

	% by measure	Sp gr. of fraction
Below 174° (water)...................	1.0	....
From 174° to 190.....................	4.4	....
From 190° to 195°...	10.8	1.0495
From 195° to 197.5....................	21.2	1.0450
From 197 1/2° to 200°.................	6.6	1.0390
From 200° to 202 1/2°.................	11.2	1.0340
From 202 1/2° to 205°.................	8.6	1.0290
From 205° to 210°....................	10.9	1.0255
From 210° to 215°....................	7.8	1.0185
From 215° to 220°....................	8.2	1.012
From 220° to 225°......	1.0	... .
Total below 225°.................	91.7	....

Residue (by difference) 9.3, containing 1.05% of hydrocarbons.

Shale-oil Creosote.

In the manufacture of hydrocarbon products from the crude oil or tar obtained by the distillation of bituminous shale, the different fractions are washed with a strong solution of sodium hydroxide (page 16 *et seq.*). On decomposing the resultant viscous liquid or "soda-tar" by dilute acid, a mixture of crude phenolic substances is obtained, usually amounting to 1.5 to 2% of the crude shale oil. The proportion and nature of the product vary with the character of the shale and the manner in which the distillation was conducted.

The "creosote" from shale oil presents a close general resemblance to the parallel products from beechwood tar and blast-furnace tar, with, however, the notable difference that creosol seems to be wholly absent. On the other hand, xylenols are present, also a cymenol, $C_{10}H_{14}O$, boiling at 237°. 3 isomeric phenols of the formula $C_{10}H_{13}OH$ appear to be present. The behaviour with reagents of the fraction distilling below 240° is described on page 359. The pyrogallic ethers boiling, respectively, at 253°, 265°, and 285°, found by Hofmann in wood-tar creosote, have also been isolated from shale creosote. Other bodies of very high b. p. are present, but these have not been fully examined.

Coal-tar Creosote and Creosote Oils.

The term "creosote oil" was formerly used to denote that portion of the distillate from coal-tar intermediate between "crude naphtha" and pitch. It is practically synonymous with the "heavy oil" or "dead oil," so called from its being heavier than water.

The name "creosote oil" is now sometimes applied to certain oils obtained by the distillation of bituminous shale and by the cooling of the waste gases from blast furnaces, and also to the bone oil produced in the manufacture of animal charcoal. All these products are decidedly different in their chemical and physical characters from the wood-tar and coal-tar products to which the name of creosote oil was first applied.

Coal-tar creosote oil commonly consists of that portion of coal-tar which distils between 200° and 300°, together with the residual oils from the manufacture of crude carbolic acid, naphthalene, and anthracene. This description, however, applies especially to the creosote oil produced in the best-managed works. In some works every

residue which cannot be used for any other purpose finds its way into the creosote oil well.

Fresh coal-tar creosote oil is greenish-yellow and highly fluorescent, the latter character being still more evident after exposure of the oil to air and light. After a time the oil becomes bottle-green by reflected and dark red by transmitted light. The smell is unpleasant and highly characteristic. When rubbed between the fingers, the feel is at first oily, but the tar acids soon act on the skin, producing a sensation of friction. Creosote oil is always somewhat heavier than water, the sp. gr. of the portions last distilling being as high as 1.10. It usually contains more or less naphthalene, phenanthrene, anthracene, diphenyl, and other solid hydrocarbons; phenol, cresols, and higher phenols; about 2% of pyridine, cryptidine, quinoline, acridine, and other substances of basic character; and the so-called indifferent oils, fluid at ordinary temperatures, and about which comparatively little is known, notwithstanding the enormous quantity of creosote oil produced (see "Naphthalene Oils").

Noelting believes that the volatile phenols of creosote oil contain, in addition to α- and β-naphthol and higher homologues of phenol, the phenols of anthracene and phenanthrene (*Ber.*, 1885, 385). The dihydric phenols characteristic of wood-tar are conspicuous by their absence.

	Sp. gr., 32°	Percentage of distillate 315°	Percentage of tar-acids from distillate
A. *Whole runnings of heavy London oils*			
Highest................................	1075	79	8.0
Lowest.................................	1048	60	3.0
Average of 20 samples................	1058.8	71.5	5.6
B. *Partial runnings of London oils*			
Highest................................	....	91	10.2
Lowest.................................	....	78	8.2
Average of 20 samples................	....	82.8	9.15
C. *English country oils*			
Highest................................	1056	90	24.0
Lowest.................................	1024	72	13.5
Average of 18 samples................	1033.5	81.8	18.6

The preceding table shows the general character of coal-tar creosote oils of different kinds. The samples under A were the *whole runnings* of heavy oils distilled from samples of tar obtained from 20 different London gas works. The samples of oil under B were produced at the works of the Gaslight and Coke Company at Beckton and represent creosote oils from which portions of the green oils and naphthalene were excluded. Hence these samples are comparatively rich in tar acids and give a larger distillate below 315° than the whole running described under A. The liquefying point of the B samples ranged from 37° to 32°, and the point of turbidity on cooling from 31° to 29°. The samples in series C were analysed by L. Archbutt. All were completely fluid at 33° and many at 15.5°. The sample yielding 72% of distillate and 13.5 of tar acids was the product of a special treatment. The samples in series C are probably somewhat richer in tar acids than the generality of country oils.

Writing in February, 1885, the late C. M. Tidy, who analysed the B samples, stated that the best London creosote oils contain a proportion of tar acids closely approximating to 8%, and he stipulated for this amount, believing it to secure the genuine character of the oil.

The dead oils made in London, and from the tar from Newcastle coal generally, are the richest in naphthalene and constituents of high b. p., but contain only a moderate percentage of tar acids. The "country oils," or oils from the Midland districts, are lighter, thinner, and more volatile than "London oil," and usually contain less naphthalene and a larger proportion of tar acids than the latter. The Scotch oils are largely derived from cannel coal, are still thinner and more volatile, and are sometimes lighter than water.

Creosote oils from coal-tar receive their main application in the creosoting or preserving of timber, and their technical assay is practically limited to an examination of their suitability for this purpose. The impregnation of wood with creosote oil chokes up the pores and materially hinders the subsequent absorption of water. The odour of creosote oil is one much disliked by the lower animals, while certain of the constituents have a powerful antiseptic action.

The following specifications for creosote for preserving timber and discussion of the subject are by S. P. Sadtler (paper read before Am. Institute of Chem. Eng., June, 1909, to be published in Vol. 2, Transactions of the Institute).

These specifications had reference to sp. gr., percentage of phenols

(or tar acids), of naphthalene allowable, and to the range of temperature within which the oil should distil. Until recently most experts valued the tar acids and naphthalene as the important constituents and demanded definite percentage of each. Now the weight of opinion is in favour of the heavy oils which come over after the naphthalene in the distillation and considers the naphthalene as of no value whatever. This is because naphthalene is volatile at all temperatures and will disappear entirely from the wood in course of time.

As illustrating the views held on the subject of the proper composition for a creosote oil for timber preservation Dr. Sadtler quotes a few foreign specifications and a few American ones of different dates:

The Belgian State Railways specify for creosote oil, "sp. gr. 1.05 at 15°, 5% tar acids, 1/3 distilling at 200°–250° and 2/3 at 250° and above."

The Western Railway of France.—"Sp. gr. minimum 1.015 at 50°, 6% acids, should be completely liquid at 40°, at 15° a minimum of 10% and a maximum of 25% solid deposit allowed."

Roumanian State Railway.—"Sp. gr. 1.05 to 1.10 at 15°, 6% to 10% phenol, 1/3 distilling at 200°–250°, 1% green oil between 288°–400°, completely liquid at 40°, 10% to 30% of naphthalene."

German Impregnating Works.—"Sp. gr. 1.02 to 1.055 to 15%, 10% to be dissolved in soda solution of 1.15 sp. gr., up to 150° nothing distilling, 150°–235° 25% as a maximum, all should distil between 150°–400°."

Letheby's English Specifications.—"5% acids, 90% should distil below 315°.

Midland Railway Co. of England.—"Sp. gr. of 1.04 to 1.065 at 90° F., not less than 25% not distilling at 600° F. (315° C) and not less than 6% tar acids."

Of these specifications, the Belgian, German, and Midland Railway Co. show the influence of the more recent views, while the others practically demand naphthalene and do not insist on the heavier oils as essential. The American specifications are all of relatively recent date and show in the main the change of views as to what is considered as desirable.

Herman von Shrenk, of the United States Forestry Bureau, in 1903 (Year-book of the Department of Agriculture for 1903, page 435) proposed the following: "The sp. gr. must be about 1.04 to 1.10 at a temperature of 20°. The b. p. must be as follows: up to 150° nothing

must come off; up to 200° not more than 10% may come off; up to 235° not more than 15% may come off; up to 355° at least 90% must come off. The oil must be soluble in benzene or in absolute alcohol."

These specifications are relatively high. In 1905, E. H. Bowser, of Louisiana, who had been practically engaged in creosoting work in that State (see Hour. Association of Eng. Societies, April, 1905), proposed: "The sp. gr. shall be not less than 1.04 at 35°; it shall not yield more than 10% by weight when distilled up to 210°; between 210° and 235° the distillation shall not be less than 25 nor more than 30% and at least 30% by weight shall not distil below 260°." These specifications were quoted with approval by H. R. Standford in a paper read before the American Society of Civil Engineers, Dec. 20, 1905.

In Circular 141 of the Forest Service, United States Department of Agriculture, entitled, "Wood Paving in the United States," the specifications of the city of Minneapolis for creosote oil for wooden block impregnation are given. These state: "The sp. gr. of the oil at 20° shall be at least 1.09; the oil shall be completely liquid at 25° and show no deposit on cooling to 22°; it shall not contain more than 2% of water, nor more than 3% of matter insoluble in absolute alcohol or benzene; on distillation, up to 150° nothing must come off, up to 170° 2%, up to 210° from 6% to 8%, up to 325° from 20% to 30%, up to 315° from 40% to 50%, up to 355° from 60% to 80%." It will be seen that this calls for a relatively heavy oil, containing high boiling fractions.

The most recent publication which deals with this subject in detail is Circular 112 of the Forest Service on "The Analysis and Grading of Creosotes," by Dean and Bateman, issued Feb. 26, 1908. The authors have studied a large number of samples of creosote oil from coal-tar as well as from other sources, and as a result of their studies propose 4 grades of creosote oil, designated, respectively, as Grades A, B, C, and D. They give the distillation curves of each of these as well as note their accordance with certain limits of sp. gr., index of refraction, and percentage of oil remaining after sulphonation test. The distillation range, as might be expected, is high for the better grade oils.

The question as to what should be the composition of a creosote oil has been attacked, however, with very satisfactory results, by extracting the oil from creosoted timber which has stood exposure for some years and examining it as to its composition. Thus, von Schrenk in 1907 in a paper read before the New England Railroad Club gives

as the result of his examination of oil extracted from creosoted timber in service from 1897 to 1906 percentage figures indicating that "during the 9 years of exposure, the naphthalene fraction has practically disappeared from the wood above the ground." In that part of the creosoted timber below the ground it had diminished but had not disappeared.

Prof. Gellert Alleman, however, has more recently published a fuller study of this question of the character of the extracted oils. He obtained these oils from railroad ties, piles, and paving blocks, in all 37 samples, which had been creosoted in both English and American practice and had been in service for periods varying from 9 to 47 years. His conclusions are as follows:

"The creosotes recovered contained practically nothing which boiled below 205°. The general average shows that 32.9% of the oils distilled below 270° and 66.95% above—that is, 2/3 above and 1/3 below this rather high temperature. Another noticeable fact is the large amount of solid anthracene oil recovered from the distillates of many samples, the highest being 57%.

A distinctive feature of the creosotes from American piles was the quantity of naphthalene which they contained. The average from this class of timbers was nearly 26% and 1 sample showed over 48%. It appears probable that the creosotes used in treating these timbers contained much more naphthalene than the oils applied to the English piles. The results indicate that this substance possesses value for timber treatment, although it probably is inferior to anthracene oil.

It is worth noting that these long-lived American piles contained more anthracene oil than naphthalene.

Perhaps the most striking thing is the disappearance of the tar acids. It is certainly conservative to place the original tar-acid content at 5%. Yet the extracted oils showed but a tenth of this amount.

It appears, therefore, that light oils, boiling below 205°, will not remain in timber, but that heavy oils, containing a high percentage of anthracene oil, will remain almost indefinitely and protect the wood from decay and boring animals. It is probable that naphthalene stays in wood for many years, but whether it is as valuable as anthracene oil is an open question. The value of the tar acids has apparently been overestimated by many persons, for although it has not been proved that they are valueless, they have been shown to possess poor staying qualities.

The preservative properties of creosote oil have been ascribed to the "tar acids," or phenolic constituents, as they are powerful antiseptics, coagulating albumin and rendering animal life impossible, but it is probable that their value has been greatly overrated, since the solubility and volatility of the lower members prevent a permanent antiseptic influence. Hence the phenolic substances of high b. p. and slight solubility may be of more value for creosoting timber than phenol and the cresols, but the lower members are doubtless valuable as coagulators of albumin, and should be present in sufficient quantity to effect this. If dissolved or volatilised from the timber, they will probably create an antiseptic atmosphere, and thus prevent the approach of living organisms. The basic constituents are also possibly of antiseptic value, and certain of them are not readily washed out or volatilised. The naphthalene of coal-tar creosote volatilises only from the superficial strata of the timber, and, by solidifying and filling up the pores of the wood, probably acts mechanically as a valuable preservative agent.

Creosote oils have also been employed as fuel, for production of illuminating gas, carburetting coal-gas, softening hard pitch, manufacturing lubricating compounds, burning for lamp-black, and production of antiseptic preparations. The so-called "Lucigen light" is obtained by projecting a spray of creosote oil by compressed air, whereby a circular brush of flame of high illuminating power is produced.

The following are analyses of 2 samples of creosote oil, one from coal-tar and one from water-gas tar, made by the reviser of this section:

	I Water-gas tar Creosote fraction	II Coal-tar creosote fraction
Sp. gr. at 60° F.................	....	....
Consistency at 60° F.............	Relatively thin liquid	Thin liquid
Consistency at 32° F.............	Still thin liquid	Thin liquid
Index of refraction (at 40°)........	1.639	1.563
Index of refraction (at 60°).......	1.6315	....
Viscosity at 100°.................	55 seconds (Engler)	47 seconds (Engler)
Sulphonation test................	2.14%	1.118%
Evaporation % 4 hours at 98°.....	10.07%	89.3%
Percentage of phenols............	None.	14%

I. DISTILLATION RESULTS WITH WATER-GAS TAR FRACTION.

Fraction	Range in temperature	Amount in c.c.		Percentage over
1	Up to 260°	17.5 c.c.	=	5.5%
2	260° to 310°	28 c.c.	=	15.2%
3	310° to 330°	36 c.c.	=	27.2%
4	330° to 350°	65 c.c.	=	48.7%
5	350° to 370°	63 c.c.	=	69.8%
6	370° to 380°	33.5 c.c.	=	81.0%
7	Residue	57 c.c.	=	19.0%
		300 c.c.	=	100.0%

	Refractive index		Sp. gr.	
	40°	60°	15°	60°
Original......................	1.6370	1.6315	1.073	1.0448
Fraction 1.....................	....	....	0.904	0.8758
Fraction 2.....................	1.5892	1.5800	1.017	0.9888
Fraction 3.....................	1.6181	1.6095	1.054	1.0258
Fraction 4.....................	1.6371	1.6288	1.074	1.0458
Fraction 5.....................	1.6540	1.6450	1.093	1.0648
Fraction 6.....................	1.6525	1.6434	1.086	1.0578

1. *a. Additional Distillation Results with Water-gas Fraction.*—1,500 c.c. of the 1.073 water-gas tar oil were distilled in iron retort and 375 c.c. collected between 160°–343°; 300 c.c. of this was fractioned in a Hempel distilling flask (thermometer exposed above 60°; temperature of stem, 40°–85°).

Fractions	Range of temperature	Amount in c.c.		Percentage over
1	160° to 200°	34.5 c.c.	=	11.5%
2	200° to 240°	24.5 c.c.	=	19.7%
3	240° to 280°	52 c.c.	=	37.0%
4	280° to 300°	54.5 c.c.	=	55.2%
5	300° to 320°	37 c.c.	=	67.5%
6	320° to 330°	27 c.c.	=	76.5%
Residue	....	70.5 c.c.	=	23.5%

	Refractive index		Sp. gr. 60°
	40°	60°	
Fraction 1........................	No film	No film	0.8537
Fraction 2........................	No film	No film	0.9124
Fraction 3........................	1.5718	1.5622	0.9716
Fraction 4........................	....	1.5872	1.009
Fraction 5........................	....	1.6006	1.029
Fraction 6........................	....	1.6165	1.018

Viscosity in Pipette at 180° F.:   (For comparison only.)
Barrett Co. creosote oil.............25 c.c. = 15 seconds
Water-gas tar fraction 1 a...........25 c.c. = 15 seconds

II. DISTILLATION RESULTS WITH COAL-TAR CREOSOTE.

Fraction	Range of temperature	Amount in c.c. Percentage over
1	Up to 200°	27.6 c.c. = 9.2%
2	200° to 210°	60 c.c. = 29.2%
3	210° to 220°	57 c.c. = 48.2%
4	220° to 230°	44 c.c. = 62.9%
5	230° to 240°	33 c.c. = 73.9%
6	240° to 260°	32.5 c.c. = 84.7%
7	260° to 280°	17.5 c.c. = 90.5%
8	280° to 295°	10 c.c. = 93.5%
9	Residue solid	18.4 c.c. = 6.5%

	Refractive index		Sp. gr.	
	40°	60°	15°	60°
Original........................	1.5630	....	1.117	1.084
Fraction 1......................	1.5340	....	0.974	0.946
Fraction 2......................	1.5540	1.5456	1.003	0.975
Fraction 3......................	1.5665	1.5537	1.021	0.993
Fraction 4......................	1.5813	1.5710	1.089	1.061
Fraction 5......................	1.5864	1.5753	1.025	0.997
Fraction 6......................	1.5929	1.5813	1.028	1.000
Fraction 7......................	1.5945	1.5854	1.037	1.009
Fraction 8......................	1.6050	1.5950	1.115	1.084

Assay of Creosote Oils.—As previously stated (page 371), the value of creosote oils for preserving timber depends on several constituents, all of which should therefore be taken into account in the examination. Unfortunately, the assay of creosote oils is often conducted according to the arbitrary conditions of a contract note drawn up without much reference to the chemical nature of the article to be assayed, or to the possibility of obtaining a fairly accurate determination of the leading constituents by the mode of operation prescribed. The early specifications often stipulated for a certain sp. gr.; the absence of a deposit when cold; the presence of a certain proportion of tar acids; the volatility of a certain percentage below 315°; and, occasionally, still more arbitrary stipulations were made. Later specifications include no reference to the sp. gr., allow the presence of a considerable proportion of naphthalene, and stipulate that a certain percentage of the oil shall not distil below a given temperature, instead of the opposite—this modification being a recognition of the value of the fractions of high b. p. No practical recognition has yet been made of the antiseptic value of the basic constituents of creosote oil nor of the fact that the portion of the oil distilling below 315° does not contain the whole of the tar acids.

The sp. gr. of creosote oil is not a criterion of its suitability for treating timber, but is an indication of genuine character of the samples: that is, their derivation from coal-tar only.

The presence of solid naphthalene in the cold creosote oil is no detriment, but the deposit should wholly dissolve on warming. A sample should become quite clear below 38°, and should not become turbid again till cooled to 32°.

The liquefying-point is usually ascertained by transferring an average sample of the oil to a test-tube, immersing a thermometer, and warming it gently till it becomes liquid. The point of turbidity is similarly observed by allowing the tube to cool spontaneously.

These simple tests are much more satisfactory than the assay for solid naphthalene, as required by the Crown Agents for the Colonies. If necessary, the approximate determination of the naphthalene may be effected in the manner carried out in the works-laboratory of Messrs. Burt, Boulton & Haywood, as follows: "100 grm. of the sample are placed in a small beaker and cooled to a freezing mixture to 4.5°. The oil is kept at that temperature for about 15 minutes, after which

it is thrown on a cloth filter, placed in a small funnel inserted in a larger one containing a freezing mixture, so that a temperature of 40° F. may be maintained during the filtration. The filter-cloth and contents are then removed from the small funnel as quickly as possible, and pressed strongly between coarse filter-paper in a copying press or vise. The pressed product is then detached from the cloth and weighed."

The following method, also employed in the works-laboratory of Messrs. Burt, Boulton & Haywood, is that usually adopted for ascertaining the behaviour of creosote oil on distillation:[1] 100 c.c. measure of the oil are gradually heated in a 4-oz. tubulated retort, by a small, naked flame surrounded by a tin-plate cylinder. A thermometer should be arranged in the retort in such a position that on the termination of the distillation the bulb shall only just touch the residual liquid. The flame is arranged so that the distillation shall occupy about 30 minutes. The distillate should be collected in a graduated glass cylinder, and the proportion of water observed at an early stage of the operation, as later on it is again more or less completely taken up by the phenolic constituents of the oil. The proportion of water in creosote oils is very variable, ranging from 1 or 2 to nearly 10%. The distillation is arrested at 315°, 321°, or other temperature, as specified in the contract note, the volume of the distillate being then observed.

For the determination of the *tar acids*, it is usual to employ the distillate obtained in the last operation. This is transferred to a stoppered flask, holding about 250 c.c., and treated with 30 c.c. of a solution of sodium hydroxide, made by dissolving 23 grm. of pure sodium hydroxide in water, and diluting to 100 c.c. The liquid is thoroughly agitated, heated for a few minutes in a water-bath, and again thoroughly agitated for about a minute. The whole is then poured into a separating funnel, the alkaline liquid drawn off, and the oil agitated with a further quantity of 15 c.c. of the solution, which is then separated as before. To ascertain if the extraction of the phenols is complete, it is necessary to agitate the undissolved portion with alkali a third time, and slightly acidify the liquid separately. Complete extraction is generally indicated by the solution ceasing to acquire a reddish tint. The alkaline liquids are mixed, well cooled, separated from any further

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[1] For the details of this and the following test, as also for much other information on creosote oils and other tar products, the author is indebted to Mr. D. Bendix.

stratum of oil, and treated with a slight excess of diluted sulphuric acid (1×3), of which about 30 c.c. will be required. The mixture is then transferred to a graduated cylinder and allowed to *cool completely*, after which the volume of tar acids is observed, the number of c.c. obtained being the % by volume of tar acids in the sample under examination. This method is substantially that prescribed by Abel and Tidy. In the specification of the Crown Agents for the colonies a 10% solution of sodium hydroxide (sp. gr. 1.125) is employed, but otherwise the process is the same.

Tidy employs 20 c.c. of alkaline solution for the second and third extractions. The tar acids are separated and redissolved in 20 c.c. of sodium hydroxide solution (20%), and 10 c.c. of water. The solution is then boiled and filtered through a funnel containing a plug of asbestos. The plug is washed with not more than 5 c.c. of boiling water, and the filtrate allowed to cool *perfectly* in a 100 c.c. measure. It is then rendered slightly acid with diluted sulphuric acid, of which about 10 c.c. will be required, allowed to stand for 2 hours till perfectly cold, when the % of tar acids is read off. The results are lower than those given by processes in which the re-solution of the tar acids is omitted, owing to their imperfect recovery from the aqueous liquid.

The foregoing modes of operation ignore such tar acids as occur in the fraction of the oil distilling about 315° to 320°, and do not ensure the complete extraction of the acids existing in the less volatile portion of the oil. The proportion of these higher phenoloic substances extractable by strong solution of sodium hydroxide from London coal-tar creosote varies from 2 to 4%. A more accurate and practical assay of creosote oil for the content of tar acids would be effected by the following process: The oil should be distilled to the point of pitching, and the whole of the distillate subjected to the treatment with solution of soda. The alkali should at first be of moderate strength (*e. g.*, 10%), but the operation should be repeated with fresh quantities of 30% solution (sp. gr. 1.34) until the extraction is complete, as shown by the separation of mere traces of tar-acids on acidifying the alkaline liquid. To cause the alkaline liquid to separate completely and promptly from the stratum of indifferent oils, an addition of petroleum spirit should be made, and the whole again agitated. The petroleum spirit acts as a solvent for the oils, and also prevents the naphthalene from solidifying or being partly dissolved by the alka-

line liquid. Instead of liberating and measuring the tar acids in a graduated cylinder, a more accurate plan is to employ a flask with a narrow, graduated neck. The layer of tar acids is brought to the zero mark by running in mercury from a burette. The tar acids thus separated are not anhydrous. They can be further examined as described in the section treating of the assay of crude phenol.

The foregoing modified method of estimating the tar acids in creosote oils by isolation and measurement is far more satisfactory than any process based on their conversion into the bromo derivatives, as the latter plan involves the knowledge or assumption of their mean molecular weight and of their exact reaction with bromine.

Although not usually practised, a valuable addition to the ordinary method of examining creosote oils consists in a determination of the basic constituents. This may be effected by distilling the sample to the point of coking and agitating the distillate with diluted sulphuric acid (1 to 3). The acid liquid is separated, rendered distinctly alkaline with sodium hydroxide, any oily layer separated, and the aqueous liquid distilled nearly to dryness. This second distillate is mixed with the oily layer, the whole acidified with hydrochloric acid, and evaporated to dryness on the water-bath. The residue consists of the hydrochlorides of the tar bases, from which the bases themselves may be liberated by solution in a small quantity of water and addition of solid sodium hydroxide to the liquid until saturated. If desired, the bases may be further examined by converting them into platino-chlorides.

Mr. Edwin M. Chance kindly submitted to the present writer the following methods, pages 377 to 380. These are the methods used in the laboratory of the Philadelphia and Reading Coal and Iron Company.

Technical Examination of Creosote Oils.—The analytical examination of so-called creosote oils designed for use in timber preservation, has for its objects the determination of the source of these oils and their physical character.

In this laboratory (Philadelphia and Reading Coal and Iron Company) these ends have been reached by making the following tests:

1. Appearance.
2. Specific gravity.
3. Melting point.

4. Flash and fire points.
5. Moisture.
6. Solubilities.
7. Volatility.
8. Tar acids.
9. Fractionation.
    a. Nature and appearance of fractions.
    b. Specific gravity.
    c. Refractive indices.
    d. Sulphonation test.

The first and most important fact to be ascertained is whether or no the oil under examination be a true creosote; if so, to determine its source and, lastly, to grade it as to quality. These questions are readily answered by an inspection of the results of the above operations. The manner of the interpretation of these results lies beyond the scope of this paper.

The actual analytical operations are extremely simple and are carried out as follows:

1. **Appearance.**—The oil (if liquid) is shaken and poured into a beaker, colour, odour, fluorescence, and any solid matter are noted.

2. **Sp. Gr.**—Determined by means of Westphal balance, or pyknometer at 60°.

3. **M. P.**—If solid at ordinary temperatures the m. p. is determined by any of the standard methods.

4. **Flash and Fire Points.**—Determined in an open copper or porcelain dish, of about 125 c.c. capacity, heated in a sand-bath, so that the temperature will rise 2° per minute. A test flame, 3 mm. in length, is applied every 1°.

5. **Moisture.**—The method of Marcusson has been found to be far superior to all others, both in point of accuracy and rapidity of operation.

50 grm. of creosote are weighed into a 250 c.c. Erlenmeyer flask. 75 c.c. of water-saturated xylol are added. A condenser is connected and the contents are distilled, by means of an oil-bath, till the distillate comes over perfectly clear. The distillate is caught either in a 50 c.c. graduated eudiometer tube, a burette filled with water to the 50 c.c. mark or, better, in a large funnel with a graduated stem, the end of which is sealed.

After distillation the receiver is set to one side, till the emulsion is

entirely broken, when the volume of water may be directly read off. Any bubbles of water adhering to the funnel in the xylol stratum may be readily gathered together by means of a glass rod, and incorporated in the main body of water. The important point in this operation is to distill slowly.

6. **Solubilities.**—The solubility in benzol, alcohol, and 88° Be. gasoline is noted, about 1 c.c. of creosote and 15 c.c. of the solvent being taken.

7. **Volatility.**—The method of Dean[1], slightly modified, is used: 5 c.c. of the oil is weighed in the tared bottom half of a Petri dish. The dish is then heated to 110° in an air-bath, and kept at that temperature for 30 minutes, then removed, covered with the top half of the dish, allowed to cool, and weighed. This operation is repeated till the dish has been in the bath for a space of 5 hours. The loss is calculated to %, and a curve plotted, the ordinate denoting % and the abscissa time.

8. **Tar Acids.**—The method of Alleman[2] is preferred. Distil 100 c.c. till the temperature reaches 420°. Extract the distillate with 3 portions of 40, 30, and 20 c.c., respectively, of hot sodium hydroxide, sp. gr. 1.15, combine the 3 portions of sodium hydroxide in a 200 c.c. graduate. Make acid with dilute sulphuric acid, allow to stand, heat to 60°, and read the volume of separated tar acids.

9. Fractionation.

It has been suggested by Dean[1] that the distillation of creosote oil may be best accomplished by the use of the Hempel bulb. The experience in this laboratory (Philadelphia and Reading Coal and Iron Company), however, has shown that with such a bulb, it is almost impossible to drive over oils of a high b. p. For this reason a distilling bulb of the following dimensions has been found most advantageous:

Volume of bulb,	500 c.c.
Diameter of neck,	3 cm.
Length of neck,	19 cm.
Height of delivery tube above bulb,	9 cm.
Length of delivery tube	40 cm.
Bore of delivery tube	7 mm.

[1] U. S. Dept. of Agriculture, Forest Service, Circular 112.
[2] U. S. Dept. of Agriculture, Forest Service, Circular 98.

As the delivery tube, owing to its length, makes an excellent air condenser, the use of other condensing apparatus is unnecessary.

The flask is counterpoised, and 250 grm. of creosote weighed into it. A thermometer, reading at least to 400°, is fitted by means of a cork, so that the bulb reaches to a point just below the opening of the delivery tube. The bulb is placed upon a wire gauze, and surrounded by an asbestos-board box. Distillation is then begun. The use of an Erlenmeyer Argand burner is recommended.

The distillation rate is regulated by means of a metronome so that 1 drop falls per second. It is sometimes necessary to warm the delivery tube with an auxiliary flame to prevent its becoming clogged by solidifying liquid. The distillate is caught in weighed 150 c.c. round, flat-bottomed flasks, and is divided into the following fractions:

Up to 170°	270°–290°
170°–205°	290°–305°
205°–225°	305°–315°
225°–235°	315°–360°
235°–245°	360°–400°
245°–255°	Above 400°
255°–270°	

These are weighed and % distilling determined, and plotted in a curve, the ordinate of which represents %, while the abscissa represents temperature. The distilling bulb is weighed and the residue calculated and its character noted.

The distillates are further examined as follows:

a. Their colour, odour, and consistency are noted.

b. Refractive indices determined by means of Abbé refractometer at 60°.

c. Sp. gr. determined at 60°/60° by means of 10 c.c. sp. gr. bottles.

d. Sulphonation Test. The fraction distilling between 305° and 315° or 315° and 360° is treated with 4 to 5 volumes of concentrated sulphuric acid, care being taken not to allow the temperature to rise sufficiently to cause carbonization. The flask is shaken repeatedly for 30 minutes, allowed to stand till cool, and then poured into a burette. After the oily layer has entirely separated, its volume is read off. The sulphuric acid is then drawn off, and the residual oil washed with water, and

shaken with a 10% solution of sodium hydroxide. The oil should dissolve if the original were true creosote.

Dean has devised a special separatory funnel which may be found convenient in the application of this test. It has a volume of about 100 c.c. The neck is drawn into a tube about 7 cm. long, and has a volume of about 5 c.c., and is graduated in 1/10 c.c.

Thanks are due to Mr. A. G. Blakeley, through whose courtesy much of this data has been secured.

The following methods are taken from circular, Forest Service, United States Department of Agriculture.

Moisture.—The creosoted wood, in the form of borings, turnings, saw-dust, or similar material, is quickly weighed and transferred to the 250 c.c. Erlenmeyer flask, and 75 c.c. of water-saturated xylol[1] added. The basin, which might well be of smaller diameter than that shown in Fig. 2, should be 2/3 full of melted paraffin or of some heavy lubricating oil, such as cylinder oil. The bath is heated and the distillation continued until the distillate comes in clear drops. At the end of the distillation the condenser should be rinsed with the stream from a wash-bottle containing xylol. After it has stood for a short time, the emulsion of water and xylol separates, giving 2 clear liquid layers. The mean of the readings at the top and bottom of the meniscus, between xylol and water, gives the volume of water, and the percentage of moisture in the wood is obtained by multiplying the water volume by 4. There are always smaller globules of water adhering to the sides of the graduate in the portion filled with xylol. These are readily scrubbed down with a piece of rubber tube on the end of a piece of glass tubing, which is better for this purpose than the rod commonly used for a "policeman."[2]

It is important that the distillation be carried on slowly to allow all the water in the wood to volatilize. The finer the wood particles, the more rapid may be the distillation. If rather coarse material is used, the distillation should not run faster than 1 drop per second.

Fractional Distillation.—The distilling vessel is a side-neck flask of Jena glass. The outlet tubes of the flask used were placed

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[1] Water saturated with xylol is readily prepared by heating a mixture of water and xylol with frequent shakings and subsequently removing the water in a separatory funnel.
    It has recently been found that xylol, only with great difficulty, can be used for the above-mentioned purpose and the Reviser is at present writing, Nov., 1909, finishing a paper on "The Determination of Moisture by Distillation," which he is sending for publication. In this paper he advocates the use of a benzine fraction boiling between 149° (300° F.) and 232° (450° F.).
[2] Americanism: a rod etc., used generally to rub off precipitates.

rather below the middle of the neck, and, to insure a good condensation and prevent the ignition of the first part of the distillate, these delivery tubes were 40 cm. long. Retorts are not used because the fractions obtained from these vessels are much less sharply defined. In place of the usual Bunsen burner, a Rogers burner is employed, as the flame is under better control and the contents of the distilling flask less likely to bump or froth. During the distillation the flask is placed on a thick asbestos board through which a hole about 1.5 in. in diameter had been cut. This asbestos sheet prevents the radiation of heat from the burner to the thermometer. A mica shield is placed around the distilling bulb whenever protection from draught is necessary.

The thermometers used are made of Jena normal glass and filled with nitrogen. To guarantee their accuracy, they are carefully compared with a set of Anschütz standard thermometers. They are always so placed that their bulbs were just below the outlet tube, so that the temperature recorded at any moment is that of the vapours passing over.

250 grm. of oil are used for each distillation. The fractions are caught in small flasks which have been previously cleaned, dried, and weighed. The amount of each distillate is determined by a second weighing taken after the fraction have cooled. When a complex mixture such as creosote is distilled the various distillates passing over do not volatilise at the exact b. p. of the individual compounds which they contain, and the compounds cannot be separated except by repeated distillations. If all creosote oils were similarly constituted, then, by means of a series of analyses, it could be readily determined at what temperatures the various constituents volatilise; but since oils vary greatly in composition, this is not possible; such temperatures as are determined upon for the separation of the various fractions are, in a measure, arbitrary. For instance, if an oil is high in naphthalene contents and also contains a certain amount of material distilling below 200°, some of the naphthalene is liable to volatilise with the lighter oil, and it will entirely have passed over when a temperature of 245° is reached. On the other hand, if the oil contains a large amount of the higher boiling constituents, such as anthracene, and also a considerable amount of naphthalene, the latter is frequently not gotten rid of before a temperature of 250° is reached. The point at which naphthalene ceases to come off, if it is present, can be determined by allowing

a drop of the distillate supposed to contain it to fall on a piece of cold porcelain. If the drop solidifies, the presence of naphthalene is shown.

In over 800 distillations it was found that 92% of those oils which contained naphthalene gave it off between 205° and 245°, and one of the fractions has frequently been taken between these temperatures.

After conducting tests on a great many oils Dean was of the opinion that the most information could be obtained by separating the distillates as follows:

1.	to 170°.	5.	270° to 320°.
2.	170° to 205°.	6.	320° to 420°.
3.	205° to 245°.	7.	Residue above 420°.
4.	245° to 270°.		

Fraction No. 1 contains the light oil and water. In case much water is present some of the naphthalene will frequently volatilise with it.

No. 2 should contain phenol and the cresols.

No. 3 contains naphthalene and the 2 methylnaphthalenes; these bodies crystallise out, and by filtration the amount of solid naphthalene can be determined.

No. 4 contains among other compounds, dimethylnaphthalenes.

No. 5 was usually entirely liquid on cooling, and its composition is complex and variable. In case little anthracene oil is present, some of it will be found in this distillate.

No. 6 usually contains anthracene oil, phenanthrene, acridine, etc., and solidifies on cooling.

The residue above 420° may contain practically the same as No. 6 and also tar.

When the distillation has reached the 225° point, an asbestos-board box should be placed around the distilling flask to cover the bulb, but leave the Hempel column exposed. Draughts upon the distilling apparatus must be avoided.

Index of Refraction.—The indices of refraction of the different fractions between 235° and 305° are determined at 60° in a refractometer with light compensation. The results are plotted with temperatures as abscissæ and indices of refraction as ordinates.

The sp. gr. of the fractions between 235° and 305° are determined by means of sp. gr. bottles. These bottles are filled at 60° and the weights referred to water at the same temperature. The results are plotted as a curve, in which the ordinates are sp. gr. at 60° and the abscissæ temperatures.

Sulphonation Test.—The fraction distilling between 305° and 320°[1] is treated with concentrated sulphuric acid and poured into a special separatory funnel, such as is shown in Fig. 10.[2] The flask which contained the fraction is rinsed out twice with concentrated sulphuric acid and the rinsings added to the funnel. Enough more concentrated sulphuric acid is then added nearly to fill the funnel, and the mixture is thoroughly shaken at least 6 times in 30 minutes. After standing until it becomes cool the volume is brought up into the graduations by the addition of concentrated sulphuric acid, and after another hour the amount of unsulphonated oil is read and the percentage calculated. The residual oil is usually almost white or a pale blue. In some cases a reddish oil with a distinctive odour is obtained from a pure coal-tar creosote; this oil does not consist of hydrocarbons and is soluble in alkali hydroxide. The sulphuric acid should, therefore, be drawn off, the oil washed with water, and a 10% solution of sodium hydroxide added. If the oil is soluble in this reagent, the sulphonation test is regarded as negative.

FIG. 10.

Tar Acids.—50 c.c. of the creosote under analysis are measured at 60° into a small distilling flask by a pipette. The oil is distilled as completely as possible without breaking the distilling bulb, and the distillate is caught in a short-stemmed, 100 c.c. separatory funnel. At the end of the distillation 25 c.c. of boiling hot 15% sodium hydroxide is added to the distillate and the mixture thoroughly shaken. The alkaline extract is then drawn off into a 100 c.c. shaking cylinder and 25 c.c. more of hot sodium hydroxide added. After extracting with this second portion for 5 minutes, with frequent shaking, the solutions are allowed to separate and the alkaline extract added to the first portion in the cylinder. A third extraction is made with 15 c.c. of alkali. The total alkaline extract is cooled, acidified with sulphuric acid, thoroughly shaken, brought to 60°, and the volume of supernatant oil is read off.

Water.—After weighing the first 2 fractions of a fractional distillation they are united in a small separatory funnel and any water which is present is separated from the oil and its amount accurately deter-

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[1] The present writer found in water gas-tar creosote that more non-sulphonatable oil was found in other fractions than between 305° and 320°. In fact the original oil contained more in proportion than this fraction.

[2] Figs 10 to 19, inclusive, are reproduced, with permission, from Circular 112, by Dean & Bateman, Forest Service, U. S. Dept. of Agriculture.

mined. If particular accuracy is required in the estimation of the water it may be done by the Marcusson xylol distillation method (Forest Service Circular 134, "The Estimation of Moisture in Creosote Wood"). (See page 381.)

Grades of Creosote.—The various methods of creosoting timber and the various purposes for which creosote timber is intended indicate so strongly the varying values of different sorts of oil that the following 4 grades are tentatively proposed.

Grade A.—On a fractional distillation, according to · the laboratory method outlined above, the distillation curve shall fall within the shaded limits shown in Fig. 11. The indices of refraction at 60° of the fractions shall not fall more
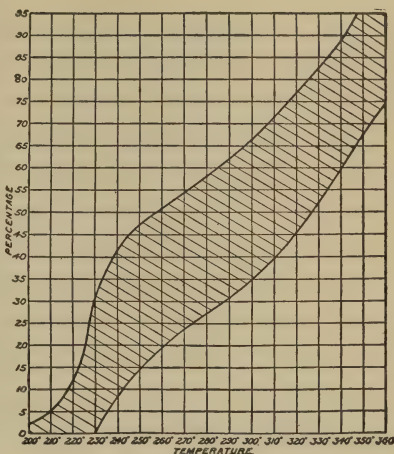
FIG. 11.

than 1 in the third place of decimals below the range in Fig. 12, and the sp. gr. at 60° shall not fall more than 1 in third place of decimals below the lower limits shown in Fig. 13. On applying the sulphonation test to the fraction between 305° and 320° there shall be no oily

FIG. 12.

residue insoluble in alkali hydroxides. The water shall not exceed 1%. There shall be no admixture of undistilled tar.
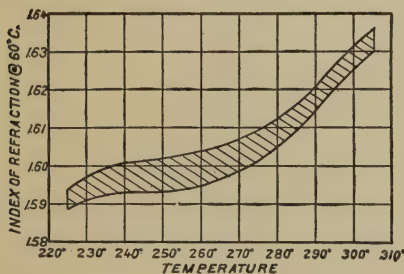
Grade B.—The percentage weights on distillation by the laboratory method shall fall within the shaded limits in Fig. 14. The specifications for index of refraction, sp. gr., and sulphonation test are the same as for Grade A. The water shall not exceed 2%. There shall be no admixture of undistilled tar.

Grade C.—The percentage weights on distillation, according to the laboratory method, shall fall within the limits shown in Fig. 15,

and the indices of refraction shall fall within the limits shown in Fig. 16. The volume of the sulphonation residue in the fraction, 305°–320°, shall not be greater than 1/10 of the weight of the fraction. The
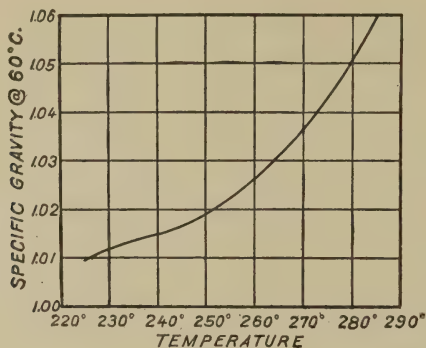
FIG. 13.

water shall not exceed 4%. There shall be no admixture of undistilled tar.

Grade D.—The distillation limits are shown in Fig. 17, and the
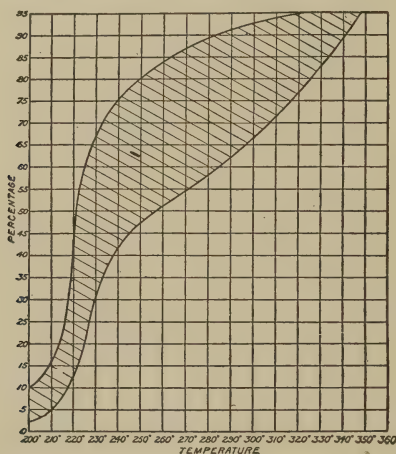
FIG. 14.

indices of refraction shall fall within the limits shown in Fig. 18. The volume of the sulphonation residue from the fraction, 305° to 320°, shall not exceed 1/5 of the weight of that fraction. The water

in the creosote shall not exceed 5%, and admixture of undistilled tar or other viscous material shall not exceed 15%.

Uses of the Various Grades.—The Grade A oil is adapted for
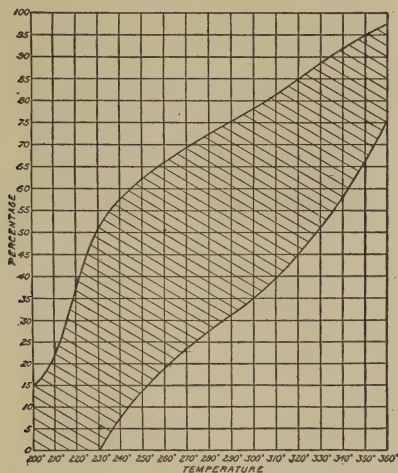
FIG. 15.

open-tank treatment or other operations where excessive loss from volatilisation is possible during the process. It should be a pure coal-tar creosote, consisting almost entirely of aromatic compounds.
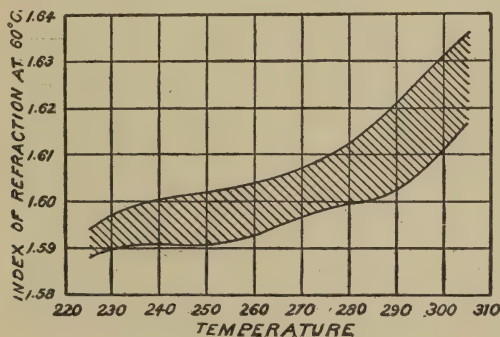
FIG. 16.

An oil of this sort is also particularly well adapted for use in processes where only a minimum quantity of the creosote is employed, such as an empty cell process, where it is essential that nearly all of the oil

used shall stay in the timber and protect it, since it is the sort of oil which would show a minimum loss by volatilisation from treated timber.
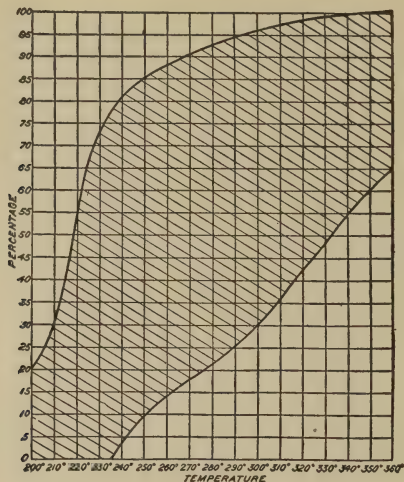
Fig. 17.

Grade B is a pure coal-tar creosote, but contains a much larger proportion of the low boiling constituents than grade A. It is well adapted for close cylinder operations and for timbers which will be protected by soil or water from excessive evaporation.
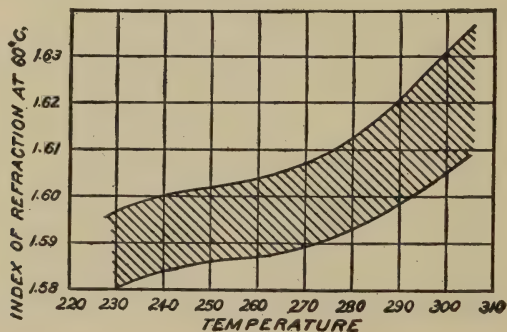
Fig. 18.

The above specifications do not include water-gas tar creosote, which is only at present writing (1909) being introduced into the market; but the analyses on page 372 show that it is made up of

high boiling aromatic hydrocarbons, and when injected into wood should remain as well as, or perhaps better than, coal-tar creosote.

Grade C allows a certain amount of added oil-tar creosote or products of a similar nature. The amount of aromatic compounds in the oil, however, would be so high that it ought to be fairly efficient as a timber preservative.

Grade D represents the poorest oils which can well be called creosotes and is not adapted for use with timbers where the minimum efficiency from impregnation is desired. Its use would be suggested for timbers where the cost of a high-grade creosote might be undesirable.

ANALYSES OF EXTRACTED OILS FROM TIMBER THAT HAS BEEN IN USE.

Samples	Average service	Creosote to the cubic foot	To 205°	Distillation of extracted oils								Tar acids
				205° to 245°	245° to 270°	270° to 320°	320° to 420°	Residue above 420°	Solid naphthalene from distillates	Solid anthralcene oil from distillates		
	Yrs.	lbs.	%	%	%	%	%	%	%	%		c.c.
19 Cross-ties............	21.84	9.58	0.05	12.07	13.88	23.80	24.69	25.27	1.19	23.47		0.65
6 English piles.......	43.00	9.19	0.46	16.92	15.31	21.06	22.77	23.04	...	19.95		..
6 American piles.....	20.20	15.64	0.57	30.28	15.82	18.49	13.21	21.43	25.93	43.27		0.61
4 Paving blocks.....	23.60	15.70	0.29	21.34	21.39	18.73	19.40	18.64	12.52	40.40		0.52
1 Paving block, poor service	9.00	5.77	9.62	14.41	19.27	41.74	11.23	3.40	...	...		..
1 Conduit pipe......	14.00	8.74	5.08	27.23	10.46	27.68	19.03	9.93	23.17	14.28		..
Average of 36 timbers giving good service..	24.90	11.18	1.36	17.37	15.18	22.00	21.71	23.09	6.98	27.81		.50

LIQUID LIGHTER THAN WATER.

TABLE FOR

COMPARISON OF SP. GR. AND BAUMÉ DEGREES.

The figures of the third column (15.5°) are according to the American Standard.

B°	12.5° 146 136+B°	15.5° 140 130+B°	B°	12.5° 146 136+B°	15.5° 140 130+B°	B°	12.5° 146 136+B°	15.5° 140 130+B°
10	1.0000	1.0000	41	0.8242	0.8187	72	0.7018	0.6931
11	0.9931	0.9929	42	0.8190	0.8139	73	0.6985	0.6897
12	0.9865	0.9859	43	0.8155	0.8092	74	0.6951	0.6863
13	0.9800	0.9790	44	0.8111	0.8045	75	0.6919	0.6829
14	0.9733	0.9722	45	0.8066	0.8000	76	0.6887	0.6796
15	0.9688	0.9655	46	0.8022	0.7954	77	0.6854	0.6763
16	0.9605	0.9589	47	0.7978	0.7909	78	0.6822	0.6731
17	0.9542	0.9523	48	0.7935	0.7865	79	0.6790	0.6699
18	0.9480	0.9459	49	0.7892	0.7821	80	0.6759	0.6667
19	0.9419	0.9395	50	0.7849	0.7777	81	0.6728	0.6635
20	0.9359	0.9333	51	0.7807	0.7734	82	0.6697	0.6604
21	0.9299	0.9271	52	0.7765	0.7692	83	0.6667	0.6572
22	0.9240	0.9210	53	0.7724	0.7650	84	0.6636	0.6542
23	0.9179	0.9150	54	0.7684	0.7608	85	0.6606	0.6511
24	0.9125	0.9090	55	0.7644	0.7567	86	0.6576	0.6482
25	0.9068	0.9032	56	0.7604	0.7526	87	0.6547	0.6452
26	0.9012	0.8974	57	0.7564	0.7486	88	0.6518	0.6422
27	0.8957	0.8917	58	0.7525	0.7446	89	0.6489	0.6492
28	0.8902	0.8860	59	0.7486	0.7407	90	0.6460	0.6363
29	0.8848	0.8805	60	0.7449	0.7368	91	0.6432	0.6334
30	0.8795	0.8750	61	0.7411	0.7329	92	0.6404	0.6306
31	0.8742	0.8695	62	0.7373	0.7290	93	0.6376	0.6278
32	0.8690	0.8641	63	0.7336	0.7253	94	0.6348	0.6250
33	0.8639	0.8588	64	0.7299	0.7216	95	0.6320	0.6222
34	0.8589	0.8536	65	0.7263	0.7179	96	0.6293	0.6195
35	0.8538	0.8484	66	0.7227	0.7142	97	0.6266	0.6167
36	0.8492	0.8433	67	0.7191	0.7106	98	0.6239	0.6141
37	0.8459	0.8383	68	0.7155	0.7070	99	0.6212	0.6115
38	0.8390	0.8333	69	0.7120	0.7035	100	0.6186	0.6087
39	0.8342	0.8284	70	0.7087	0.7000	101	0.6160	0.6060
40	0.8295	0.8235	71	0.7053	0.6965	102	0.6134	0.6034

AROMATIC ACIDS.

BY EDWARD HORTON, B. Sc.

The true aromatic acids form a well-defined and important group of substances containing a benzene-nucleus. Many of them occur ready-formed, either free or combined, in resins, balsams and essential oils, as well as in animal organisms; many are prepared synthetically from constituents of coal-tar. The most important series of aromatic acids bears the same relation to benzene and its homologues as the aliphatic acids bear to methane and its homologues (paraffins), and the 2 series of acids present many points of resemblance. Just as acetic acid may be regarded as the type of a fatty or aliphatic acid, so benzoic acid is representative of the aromatic or cyclic acids; whilst a parallel to acrylic acid may be found in cinnamic acid, to glycollic and lactic acids in salicylic acid, to succinic acid in phthalic acid, and so on. The following tabular arrangement renders these analogies more evident:

Fatty (aliphatic) acids	Aromatic (cyclic) acids
Formic.....................H.COOH Acetic....................CH$_3$.COOH Propionic..............C$_2$H$_5$.COOH	Benzoic (phenyl-formic)...........C$_6$H$_5$.COOH Toluic.......................C$_7$H$_7$.COOH Xylic........................C$_8$H$_9$.COOH
Acrylic................C$_2$H$_3$.COOH	Atropic (α-phenyl-acrylic) $\Big\}$ Cinnamic (β-phenyl-ac- $\Big\}$ ..C$_6$H$_5$.C$_2$H$_2$.COOH rylic)
Propiolic............... C$_2$H.COOH	Phenyl-propiolic .... C$_6$H$_5$.C$_2$.COOH
Glycollic............CH$_2$(OH).COOH	Salicylic(hydroxybenzoic)......C$_6$H$_4$(OH).COOH
Glyoxylic...........CH(OH)$_2$.COOH	Protocatechuic (dihydr- $\Big\}$ ....C$_6$H$_3$(OH)$_2$.COOH oxybenzoic)
Erythric.......... C$_3$H$_4$(OH)$_3$.COOH	Gallic (trihydroxybenzoic) C$_6$H$_2$(OH)$_3$.COOH
Succinic ....C$_2$H$_4$: $\Big\{$ COOH COOH	Phthalic ....C$_6$H$_4$: $\Big\{$ COOH COOH

All, or nearly all, the aromatic acids in the foregoing table may be extracted by ether from their aqueous solutions. When heated with lime, they split up into carbon dioxide and benzene, hydroxybenzene, or homologues or analogues thereof. Thus:—

Phthalic acid............$C_8H_6O_4 = CO_2 + C_7H_6O_2$, Benzoic acid.
Benzoic acid............$C_7H_6O_2 = CO_2 + C_6H_6$,   Benzene.
Toluic acid.............$C_8H_8O_2 = CO_2 + C_7H_8$,   Toluene.
Cinnamic acid...........$C_9H_8O_2 = CO_2 + C_8H_8$,   Cinnamene.
Salicylic acid...........$C_7H_6O_3 = CO_2 + C_6H_6O$,   Phenol.
Cresotic acid...........$C_8H_8O_3 = CO_2 + C_7H_8O$,   Cresol.
Protocatechuic acid.......$C_7H_6O_4 = CO_2 + C_6H_6O_2$, Catechol.
Gallic acid..............$C_7H_6O_5 = CO_2 + C_6H_6O_3$, Pyrogallol.

In connection with the true aromatic acids, all of which contain 1 or more carboxyl-groups, CO.OH, the phenolsulphonic acids and certain allied compounds may be conveniently considered.[1] The chief aldehydes, salts, and esters of the aromatic acids are also described in this section, as also are related substances, such as saccharin and acetophenone. The various substances are classified under the following groups:

Sulphonated Phenols and their Allies.
Benzoic Acid and its Derivatives.
Cinnamic Acid and its Derivatives.
Salicylic Acid and its Allies.
Protocatechuic Acid and its Allies.
Gallic Acid and its Derivatives.
Phthalic Acids.

SULPHONATED PHENOLS AND THEIR ALLIES.

By the action of concentrated sulphuric acid, phenol may be converted into compounds in which 1 or more of the hydrogen atoms of the benzene-nucleus are replaced by SO_3H groups. The *sulphonic acids* thus obtained usually form soluble barium salts, and hence may be separated from any sulphuric acid which has not entered into the reaction by treating the aqueous solution of the product with excess of barium carbonate and filtering.

The phenol-sulphonic acids may also be conveniently separated

[1] Except the sulphonic acids and quinolinic acid (which is a member of the heterocyclic group), all the acids described in this chapter are members of the true hexacarbocyclic series.

from the crude product by diluting this with water and saturating the liquid with common salt, when the sulphonic acids separate out as crystalline sodium salts, which may be purified by recrystallisation.

The homologues of phenol, the dihydroxy and trihydroxy phenols, and other analogous substancês, also form sulphonic acids by treatment with concentrated sulphuric acid, the resultant compounds all being split up with formation of the original phenolic substances when heated with concentrated hydrochloric acid at a temperature between 100° and 200°. This general reaction is valuable, as the various isomerides and homologues may usually be separated with comparative facility by fractional crystallisation in the form of salts of their respective sulphonic acids, and the phenols then regenerated by treating these sulphonates with hydrochloric acid.

PHENOL SULPHONIC ACIDS.

When phenol is treated with concentrated sulphuric acid it is converted into a mixture of sulphonic acids, the composition of which varies with the conditions (Kekulé, *Ber.*, 1869, **2**, 330; Engelhard and Latschinow, *Zeitsch. Chem.*, 1868, **4**, 77; Post, *Ber.*, 1875, **8**, 1547; Obermiller, *Ber.*, 1907, **40**, 3623). To obtain the ortho-acid the reaction is carried out at the ordinary temperature, but even under the most favourable conditions 3 parts of the para- are formed with every 2 parts of the ortho-acid, whilst a considerable amount of the phenol remains unattacked (Obermiller). By working at 100° to 110° the phenol-*o*-sulphonic acid is almost completely transformed into the para-isomeride. A small quantity of the meta-acid is also formed and, in the presence of a large excess of sulphuric acid, some phenol 2:4-disulphonic acid is produced.[1]

The ortho- and para-acids are most readily separated by the fractional crystallisation of their barium and magnesium salts. (Obermiller.)

The following table shows the characters of the 3 isomeric phenol-monosulphonic acids and some of their salts:

[1] Similar series of substances, the cresol and xylenol-sulphonic acids, are obtained by the action of strong sulphuric acid on cresol (Claus and Kraus, *Ber.*, 1887, **20**, 3089; Hantke, *ibid.*, 3209) and xylenols, respectively. In the sulphonation of *m*-cresol, whatever the conditions, only one *mono*-sulphonic acid is obtained. By employing a larger proportion of sulphuric acid a *di*-sulphonic acid is formed, and by heating the cresol to 180° with fuming sulphuric acid, a *tri*-sulphonic acid is produced. When *o*-cresol is heated with sulphuric acid to 100° only *o*-cresol-*p*-sulphonic acid is formed, but at the ordinary temperature *o*-cresol-*m*-sulphonic acid is also produced. When the concentrated aqueous solution of the latter acid is heated, it is converted into the former acid.

	Ortho-acid $C_6H_4\begin{cases}OH^{(1)}\\SO_3H^{(2)}\end{cases}$	Meta-acid $C_6H_4\begin{cases}OH^{(1)}\\SO_3H^{(3)}\end{cases}$	Para-acid $C_6H_4\begin{cases}OH^{(1)}\\SO_3H^{(4)}\end{cases}$
Free acid..........	At ordinary temperature, liquid; sp. gr. 1.400. Crystallises at 8° to 10°, and boils at 130°.	Crystallises in fine needles containing $2H_2O$.	Syrupy liquid; or hydrated, highly deliquescent needles.
Potassium salt.....	Melts at 240°, resolidifying to a vitreous mass. Long, flat prisms containing $2H_2O$. Very soluble.	Melts at 200° to 210°. Confused efflorescent microscopic needles or scales containing $1H_2O$	Melts at 400°. Anhydrous elongated hexagonal tables. Moderately soluble.
Sodium salt........	Indistinct crystalline masses containing $1\ 1/2\ H_2O$	Flat needles or rhombic tables containing $1H_2O$	Long prisms containing $2H_2O$
Barium salt.......	Indistinct crystalline masses containing $2H_2O$. Very soluble.	Small aminæ of microscopic needles containing $1/2\ H_2O$ Easily soluble.	Long silky matted needles containing $3H_2O$.
Lead salt..........	Indistinct tables containing $1H_2O$. Very slightly soluble.	Large rhombic tables containing $3H_2O$	Long bundles of needles containing $2H_2O$. Basic salt nearly insoluble.
Cupric salt.........	Pale blue prisms.	Thin bright green rhombic prisms containing $6H_2O$.	Deep blue plates, resembling cupric sulphate. Contains $10H_2O$.

The phenol-sulphonic acids are very stable substances and are not decomposed by boiling with alkali hydroxides.

By heating the free phenol-sulphonic acids or their salts with hydrochloric or dilute sulphuric acid under pressure, they are all decomposed completely with more or less facility, phenol being reproduced: $C_6H_4(OH)SO_3K + H_2O = C_6H_5.OH + KHSO_4$.

PHENOL-o-SULPHONIC ACID.

This substance has been employed as an antiseptic under the names *aseptol*, *sozolic acid*, and *sulphocarbol*, but Obermiller (*loc. cit.*) states that aseptol, which is sold as a 33% aqueous solution of phenol-o-sulphonic acid, really consists of a solution of the impure para-acid containing about 6% of the ortho-acid.

When the potassium salt is heated with potassium hydroxide at 250° it yields catechol. Contrary to Kekulé's statement, Obermiller finds that phenol-o-sulphonic acid is not converted into the para-acid on boiling its aqueous solution. It has very little corrosive action, is practically non-poisonous, and is said to have an antiseptic action 3 times as powerful as that of phenol, whilst the sodium salt is still more energetic.

PHENOL-*m*-SULPHONIC ACID.

A small quantity of this acid is stated by Obermiller to be formed in the direct sulphonation of phenol. In quantity it is prepared by heating benzene-*m*-disulphonic acid with aqueous potassium hydroxide solution at 170–180° (*Ber.*, 1876, **9**, 969).

When heated at 250° with potassium hydroxide phenol-*m*-sulphonic acid gives resorcinol.

PHENOL-*p*-SULPHONIC-ACID. SULPHOPHENIC ACID.

This acid, known also commercially as sulphocarbolic acid, is a powerful antiseptic and its solutions coagulate albumen. By heating it at 250° with potassium hydroxide, phenol-*p*-sulphonic acid is converted not into quinol but into resorcinol. When oxidised with manganese dioxide and sulphuric acid it yields quinone.

Sodium phenol-p-sulphonate, $NaSO_3.C_6H_4.OH$, is prepared by double decomposition from the barium salt, and is the sodium sulphocarbolate of the Pharmacopœias.[1] It forms transparent rhombic crystals containing $2H_2O$, which are readily soluble in water, and have a cooling, saline, slightly bitter taste. The salt is permanent in the air, but becomes anhydrous at 100°. At a higher temperature it evolves phenol and leaves a residue of sodium sulphate and sulphite amounting to 30.6% of the weight of the crystallised salt.

Aluminium phenol-p-sulphonate, $Al[O.SO_2C_6H_4OH]_3$ may be prepared by double decomposition. It is very soluble in water, alcohol, and glycerol, and the solutions can be kept unchanged. The salt has been introduced under the name of *"Sozal"* as a material for antiseptic dressings.

Zinc phenol-p-sulphonate forms transparent efflorescent prisms or plates containing $7H_2O$ ($8H_2O$, United States Pharmacopœia, eighth Rev.). It also occurs as a white powder. It should leave 15.08% (14.6%, United States Pharmacopœia, eighth Rev.) of zinc oxide on strong ignition. The probable impurities are *sulphates, chlorides,* compounds of the *light metals,* and free *phenol.* If prepared by the British Pharmacopœia process, a notable quantity of sulphate is certain to be present.[2]

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[1] Sodium phenol sulphonate, United States Pharmacopœia, eighth Rev.

[2] The British Pharmacopœia of 1885 directed the salt to be prepared "by heating a mixture of carbolic acid and sulphuric acid, saturating the product with oxide of zinc, evaporating and crystallising." The solution of the product was stated to be "only rendered faintly turbid" by barium chloride. The description in the B. Pharmacopœia of 1898 is even more discreditable, for whilst omitting the words "evaporating and crystallising," it describes the product as giving "only the slightest reactions with the tests for sulphates."

Reactions of the Phenolsulphonic Acids and Phenolsulpho-nates.—The salts of all 3 phenolsulphonic acids give a deep purple colour with ferric chloride solution. The colour is discharged by acids. The same reaction is observed with salicylic acid and its salts.

When a solution of phenol-*p*-sulphonic acid is boiled for some minutes with an equal volume of strong nitric acid and the solution neutralised with potassium hydroxide solution, a yellow colour due to the formation of potassium picrate, is produced. In this way 1 part of the acid can be detected in 50,000 parts of water. Phenol gives the same reaction.

Addition of bromine to a solution of phenol-*p*-sulphonic acid or 1 of its salts gives a precipitate of tribromophenol. Although phenol itself gives this reaction, the liberation of sulphuric acid from the sulphonic acid enables this to be detected in the presence of phenol.

The phenol-*p*-sulphonates may be recognised by the tests for phenol-*p*-sulphonic acid already described. The phenol-*p*-sulphonates of the alkalies if ignited alone, or those of other metals if ignited with sodium carbonate, leave a residue containing sulphate. This reaction, the formation of sulphate by treatment with bromine or boiling with nitric acid, and non-extraction by ether from acidified solutions are characters which distinguish the phenol-*p*-sulphonates from salicylates.

The presence of unconverted *phenol* in phenol-*p*-sulphonates may be detected by acidifying the solution with dilute sulphuric acid and agitating the liquid with ether or chloroform. The phenol left on spontaneous evaporation of the ether may be detected by its odour and by the yellow colour developed on warming with nitric acid and then neutralising with potassium hydroxide. A faint colour should be neglected, as it may be due to a trace of phenol-*p*-sulphonic acid dissolved by the ether.

The barium, calcium, and lead salts of phenolsulphonic acid are more or less soluble. Hence sulphuric acid and *sulphates* may be readily detected and estimated by addition of barium chloride to the original solution. *Barium* and *calcium* salts may be detected in phenolsulphonates by dilute sulphuric acid and ammonium oxalate, respectively.

Estimation.—The estimation of phenol-*p*-sulphonic acid may be based on the reaction with nitric acid, the sulphuric acid produced

being precipitated and weighed as barium sulphate and thence the weight of sulphonic acid calculated.

According to Hübener (*Chem. Zeit.*, 1908, **32**, 485) the reaction of bromine with phenolsulphonic acid is incomplete. But by boiling the sulphonic acid with a saturated solution of bromine in hydrochloric acid the sulphonic group is completely eliminated and may be estimated in the filtrate (the tribromophenol is removed by filtration) in the usual way.

Obermiller gives the following directions (*Ber.* 1909, **42**, 4361). The phenolsulphonate (0.2 to 0.3 grm.) together with 0.6 to 1.0 grm. or barium chloride is dissolved in 100 c.c. of water containing 10 c.c. of hydrochloric acid (sp. gr. 1.19). The liquid is heated to between 60° and 65° and slowly treated with a solution containing 1 grm. of potassium bromate and 5 grm. of the bromide per 100 c.c., until a faint persistent yellow colour is produced. A small quantity of an alcoholic solution of phenol is added to remove the excess of bromine, and then sufficient alcohol to dissolve the tribromophenol. The liquid is boiled and decanted whilst hot from the barium sulphate, which is repeatedly washed by decantation with 59% alcohol, and then with water. It is finally filtered and weighed.

PHENOLPOLYSULPHONIC ACIDS.

By digesting phenol at 100° with a considerable excess of fuming sulphuric acid, phenol 2 : 4-disulphonic acid is produced, whilst phenol 2 : 4 : 6-trisulphonic acid is formed when phenol is heated under pressure with sulphuric acid and phosphorus pentoxide.

The polysulphonic acids give a deep red colour with ferric chloride solution.

Phenol 2 : 4-disulphonic acid is employed in Grandval and Lajoux's method (*Compt. rend.*, 1885, **101**, 62) of estimating nitrates in water. (Compare also Gill, *Tech. Quarterly*, 1894, **7**, 55.)

A sodium mercuric phenol, 2:4-disulphonate, said to have the constitution $C_6H_3(OHg)(SO_3Na)_2$, is used under the name *Hermophenyl* as an internal antiseptic.[1]

[1] *Cosaprine* is the sodium salt of the sulphonic acid of acetanilide. It has the constitution $C_6H_4(NH.CO.CH_3)(^1)SO_3Na)(^4)$ and may be regarded as sodium phenol-*p*-sulphonate in which the hydroxyl-group has been replaced by an acetamino-group. It is an odourless, white, amorphous powder, of saline taste. It is a strong antipyretic, and presents the practical advantage of being readily soluble in water. Its solution should give no precipitate with barium chloride.

IODOPHENOL-*p*-SULPHONIC ACIDS.

When 1 molecule of iodine (in the form of a mixture of potassium iodate and iodide) is added gradually to 1 molecule of potassium phenol-*p*-sulphonate dissolved in excess of dilute hydrochloric acid, iodine at first separates, but is quickly reabsorbed, and after a short time the liquid sets to a dense mass of long thin prisms of *potassium 2:6: diiodo-phenol-4-sulphonate*, $C_6H_2I_2(OH).SO_3K + 2H_2O$. This salt requires about 50 parts of water for solution, and when heated decomposes without melting at about 270°, with evolution of violet vapours of iodine. It yields with potassium hydroxide an extremely soluble basic salt, $C_6H_2I_2(OK).SO_3K$. The *sodium salt* (normal) forms a white crystalline powder containing $2H_2O$, and is infusible at 200°. It is odourless, has a faintly acid taste, is soluble in 13 parts of cold water and more readily in hot, and is also soluble in alcohol. The magnesium, aluminium, zinc, and lead salts are readily soluble in water and glycerol, but the silver and mercury salts are but slightly soluble. The *barium salt* is only slightly soluble in cold water, from which it crystallises in white glistening needles. The *zinc salt* forms long colourless needles, and the *copper salt* pale green monoclinic prisms.

2 : 6-Diiodo-phenol-4-sulphonic acid is prepared commercially in the free state by treating diiodobenzene with fuming sulphuric acid, saturating the diluted liquid with lead carbonate, filtering, and decomposing the soluble lead salt by hydrogen sulphide. On concentrating the filtered liquid, the acid is deposited in crystals which melt at 120° and decompose at 190° with liberation of iodine.[1]

Diiodophenolsulphonic acid ($+3H_2O$) contains 52.9% of iodine, is odourless, and is a useful substitute for iodoform. Both the free acid and its salts possess well-marked antiseptic properties and are employed in medicine under the name of "*Soziodol*." "Easily soluble soziodol" is the sodium salt, and is commonly given in solution, whilst the potassium salt forms the "difficultly soluble" modification (*Pharm. J.*, 1888, [iii], **18**, 538, 621, 1006). The potassium and zinc salts are used in ointments. The mercury salt has been employed as a hypodermic injection in cases of syphilis.

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[1] In preparing the diiodo-acid, a certain amount of mono-iodophenolsulphonic acid is produced. This substance forms thick, colourless, rhombic crystals, and yields barium and calcium salts which are readily soluble in water.

PHENYLSULPHURIC ACID. PHENYL HYDROGEN SULPHATE.

$$C_6H_6SO_4; \; i. \; e., \; (C_6H_5)HSO_4; \; or \; SO_2 \Big\langle \begin{array}{l} OH \\ OC_6H_5 \end{array}$$
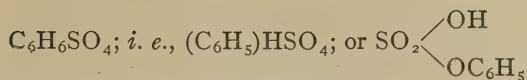
This acid is isomeric with the phenol-monosulphonic acids, C_6H_4-$(OH)SO_3H$. It occurs together with its homologue cresyl-sulphuric acid, $(C_7H_7)HSO_4$, as a potassium salt in the urine of the horse and other herbivora. These salts also occur in considerable quantity in human urine after taking carbolic acid, and traces are normally present. During exhibition of phenol the inorganic sulphates ordinarily present in urine are greatly reduced in amount or even wholly disappear, being converted into phenyl-sulphates. The quantity of sulphur existing in normal human urine in the form of phenolic and other ethereal sulphates averages one-tenth of that present as metallic sulphates. The ethereal sulphates are represented by the potassium salts of phenyl-sulphuric acid, indoxyl-sulphuric acid, skatoxyl-sulphuric acid[1] and similar compounds of catechol and quinol. E. Baumann (*Ber.*, 1876, **9,** 55) has shown that if the inorganic sulphates be first precipitated by acidifying the urine with acetic acid and warming the diluted liquid with excess of barium chloride, the filtered liquid will contain any cresyl-sulphates and phenyl-sulphates which may be present. On strongly acidifying the filtrate with hydrochloric acid and boiling it for 1 hour the phenolic sulphates will be decomposed, barium sulphate being precipitated together with resinous matter, from which impurity it may be freed by washing with hot alcohol.[2] On subsequently distilling the acidified urine the distillate contains distinct traces of phenol, directly recognisable by the bromine test (See p. 298), and if the distillate be shaken with ether and the ethereal solution separated and cautiously evaporated, the residue gives a distinct blue colouration with ferric chloride (Vol. 3). On the contrary, from the original urine no phenol can be extracted by agitation

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[1] These compounds are fully described in Vol. 7.

[2] If the filtrate be evaporated to dryness, and the residue fused with nitre, an additional quantity of sulphuric acid is formed corresponding, in human urine, to 10–20% of the total sulphur excreted, but rising in anomalous cases to a larger proportion. The unoxidised sulphur exists in the urine partly in the form of cystin, a substance having the composition $C_6H_{12}N_2S_2O_4$; but a portion is excreted in the form of thiocyanates.

with ether, a behaviour evidently due to the fact that the phenyl-sulphates are not decomposed till the urine is heated with acid.[1]

Baumann (*loc. cit.*) has actually isolated potassium phenyl-sulphate from horses' urine by the following process: The liquid is evaporated at a low temperature, the residue extracted with alcohol, and the filtered liquid concentrated to a syrup and allowed to stand in a very cold place. The crystalline plates which form are filtered off, dried, and purified by recrystallisation from strong spirit. The pearly-white tables obtaned consist of potassium phenyl-sulphate. L. Brieger treats fresh urine with neutral acetate of lead in excess, filters, and treats the filtrate with basic lead acetate. The lead is removed from the filtered liquid by hydrogen sulphide, and the filtrate evaporated to a thick syrup and kept for some time in a vacuum. The potassium phenyl-sulphate forms plates which are recrystallised from hot absolute alcohol (*Zeit. physiol. Chem.*, 1884 [iv], **8**, 311).

Potassium Phenyl-sulphate, $(C_6H_5)KSO_4$, may also be prepared by the action of potassium phenoxide on potassium pyrosulphate: $(C_6H_5)OK + K_2S_2O_7 = K_2SO_4 + (C_6H_5)KSO_4$. It crystallises in transparent rhombic tablets which feel greasy to the touch. It is readily soluble in water and sparingly soluble in cold absolute alcohol, but dissolves somewhat more readily in boiling alcohol. The aqueous solution exhibits a fine blue fluorescence.

Potassium phenyl-sulphate decomposes on exposure to moist air, sometimes in a few minutes, into phenol and potassium hydrogen sulphate. A similar change occurs by boiling the aqueous solution for a few hours or warming it for a few minutes with dilute hydrochloric acid, but it is not affected by acetic acid. On the other hand, potassium phenyl-sulphate is stable in presence of alkalis, and is only gradually attacked by potassium hydroxide at 150°. When the solid salt is heated to 150°–160° in absence of moisture it is converted into the isomeric potassium phenol-*p*-sulphonate.

Phenyl-sulphates are readily distinguished from phenol-sulphonates by the formation of phenol and a sulphate on heating the solution with hydrochloric acid. When solid potassium phenyl-sulphate is quickly

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[1] E. Davies has described a specimen of urine passed by a person recovering from poisoning by carbolic acid (*Pharm. J.*, 1883, (iii), **14**, 473). It was almost black in colour, and on distillation with sulphuric acid gave a distillate containing both phenol and cresol. The phenol was recognised by the odour, the reaction with ammonia and sodium hypochlorite, and the formation of an abundant precipitate of tribromophenol (of characteristic crystalline form) and (tri) bromocresol on adding bromine. Only a trace of phenol distilled over when the addition of sulphuric acid was omitted, and no phenol could be extracted by ether.

heated to fusion, and then dissolved in water, the solution gives a ruby-red colour with ferric chloride.

Free phenyl-sulphuric acid is so unstable that its aqueous or alcoholic solution decomposes almost immediately. It has never been isolated.

NAPHTHOL SULPHONIC ACIDS.

The practical application of the various acids obtained by the sulphonation of α- and β-naphthol is chiefly confined to the production of colouring-matters. Hence their preparation and characters are described in Vol. 5.

Asaprol or Abrastol is calcium β-naphthol-α-sulphonate, $[C_{10}H_6-(OH)(SO_3)]_2Ca+3H_2O$. It forms an odourless, crystalline, bitter powder, neutral in reaction, and soluble in water and alcohol, but not in ether. Asaprol is non-toxic, and is recommended (in doses of 4 grm.) as an antithermic in typhoid fever and articular rheumatism. It is also used as a clarifier and antiseptic in wines (see also **p. 259**).

Qualitative Tests and Detection.—The following reactions are described by Vitali (*Boll. chim. farm.*, 1908, **47**, 291). Abrastol gives a red colour with mercuric nitrate, a fine green fluorescence when treated with sulphuric acid and formaldehyde, a blue colour with Froehde's reagent, and a green tint with the vanadium-sulphuric acid reagent, all of which reactions can be observed with 0.0001 grm. of the substance. A solution of abrastol (0.1%) gives a blue colour with ferric chloride solution, a green colour with a blue fluorescence when chlorine water and a little ammonia are added, and an intense red colour changing to violet when the residue from the evaporation of 1 c.c. is treated with potassium nitrate solution and excess of sulphuric acid. Potassium nitrate solution gives a yellow colour which changes to green on evaporation and to blood-red on adding sulphuric acid. When evaporated to dryness with mercurous nitrate solution 1 c.c. of a 0.01% solution of abrastol leaves a residue having a fine violet-red colour. Abrastol gives a yellow colour with sulphuric acid and, in very dilute solution, a fine blue fluorescence with alkalies.

According to Salomone (*Giorn. Farm. Chim.*, 1906, **55**, 481) a solution of abrastol, when treated with red fuming nitric acid, gives a ruby-red colouration not extracted by ether or chloroform. After some hours, or immediately on adding alkali, the colour changes to yellow. With a solution containing only 1 part of abrastol in 300,000

of water the reaction appears after a few minutes, especially if the liquid is warmed at 40 to 50°. If a small crystal of sodium hyposulphite is added the red colour changes to blue, violet, dark-green, and finally yellow, whilst with a crystal of sodium sulphite it changes immediately to yellow. Addition of stannous chloride solution, followed by a few drops of hydrogen peroxide or ammonium persulphate solution, changes the ruby-red colour to a reddish-violet which is intensified by adding sulphuric acid.

To detect abrastol in wines, Salomone extracts 25 to 50 c.c. of the sample with 15 to 30 c.c. of amyl alcohol containing a little ammonia, evaporates the extract, and tests the residue as above. Or the residue may be fused with sodium, the product dissolved in water, and the solution tested for alkali sulphide with sodium nitroprusside (distinction from naphthol).

To detect asaprol or abrastol in red wine, A. Sanna Pintus (*Staz. sper. agrar. ital.*, 1900, **33,** 274) shakes 10 c.c. of the cold sample with 2 grm. of animal charcoal, and adds to the filtered liquid an equal volume of a solution of mercuric nitrate containing nitrous acid (prepared by dissolving 10 grm. of mercury in 9.7 c.c. of nitric acid of 1.42 sp. gr. and adding 3.5 c.c. of water to the solution). In the presence of abrastol, an immediate yellow colouration, with a golden fluorescence, is produced, the colour changing to rose on exposure to the air for a few minutes. In the case of white wines the preliminary treatment with animal charcoal is unnecessary, and the test in that case is capable of detecting 0.01% of the antiseptic. (See page 259.)

Gabutti (*Staz. sper. agrar. ital.*, 1904, **37,** 234) states that 0.1 grm. of abrastol in 1 litre of wine can be detected by extracting 100 c.c., previously made alkaline with a few drops of ammonia, with 10 to 15 c.c. of amyl alcohol, filtering and evaporating the alcoholic extract, dissolving the residue in phosphoric acid (sp. gr. 1.7), heating with a few drops of concentrated formaldehyde solution, and filtering. In the presence of abrastol, the filtrate shows a green fluorescence.

According to Carletti (*Boll. chim. farm.*, 1909, **48,** 223) when a solution of as little as 0.00005 grm. of abrastol in concentrated sulphuric acid is treated with a few drops of a 10% aqueous or alcoholic solution of tartaric acid and gently warmed, an emerald-green colouration is produced. This reaction has the advantage over that with ferric chloride of being unaffected by organic acids.

Other methods of detection are described by Sanglé-Ferrière (*Compt.*

rend., 1893, **117,** 796), Sinabaldi (*Monit. Scient.*, 1893, **7,** 842), and Briand (*Compt. rend.*, 1894,, **118,** 925). (See p. 259.)

HYDROXYQUINOLINE SULPHONIC ACIDS.

Several sulphonated compounds derived from quinoline have been recently recommended as internal antiseptics. The following are the more important of these preparations:

Diaphtol or Quinaseptol, $C_9H_5N(OH)(SO_3H)$.
Diaphterine or Oxyquinaseptol, $(C_9H_6N.OH)_2.C_6H_4.OH.SO_3H$.
Hydrargyraseptol, $C_9H_5N(OH)SO_3Hg+2NaCl$.
Loretine, $C_9H_4IN(OH)SO_3H$.

Diaphtol is hydroxyquinoline-3-sulphonic acid, diaphterine is a compound of 2-hydroxyquinoline (2 mols.) with phenol-*o*-sulphonic acid (1 mol.), while the last of the above compounds is a 3-iodo-2-hy-droxy-quinoline sulphonic acid. It forms an odourless, yellow powder, insoluble in water and only slightly soluble in alcohol, ether, or oils. The sodium salt, known as "*soluble loretine*," dissolves in water with orange colouration. Both this compound and the free acid are powerful antiseptics used in surgery.

BENZOIC ACID AND ITS DERIVATIVES.

Benzoic acid is the central member of a group of highly interesting bodies, a considerable number of which possess more or less practical interest. They all contain the radical *benzoyl*, $C_7H_6O = C_6H_5.CO = Bz$, either intact or substituted.[1] In the following compounds the benzoyl radical exists intact:

Benzoic acid (phenyl-formic acid) ....$C_6H_5.CO.OH$
Benzoyl chloride (benzoic chloride)...$C_6H_5.CO.Cl$
Benzoyl hydride (benzaldehyde)......$C_6H_5.CO.H$
Benzoyl methide (acetophenone) .....$C_6H_5.CO.CH_3$
Benzoyl-glycocoll (hippuric acid).....$C_6H_5.CO.NH.CH_2.CO.OH$
Benzoyl-ecgonine.................$C_6H_5.CO.C_9H_{14}NO_3$
Benzoyl-methylecgonine (cocaine)....$C_6H_5.CO.C_9H_{13}(CH_3)NO_3$
Benzoyl-acetyl-aconine (aconitine)...$C_6H_5.CO.(C_2H_3O)C_{25}H_{39}NO_9$

In the following allies of benzoic acid substitution occurs in the benzoyl radical itself:

[1] A colour reaction for the detection of the benzoyl group in organic compounds has been described by G. Denigés (*Analyst*, 1899, 24, 268). The indications are of very doubtful value.

Methylbenzoic acids (toluic acids)................$C_6H_4(CH_3).CO.OH$
Hydroxybenzoic acids (salicylic acid, etc.).......$C_6H_4(OH).CO.OH$
Dihydroxybenzoic acids (protocatechuic acid)....$C_6H_3(OH)_2.CO.OH$
Trihydroxybenzoic acids (gallic acid, etc.).......$C_6H_2(OH)_3.CO.OH$
Carboxylbenzoic acids (phthalic acids)..........$C_6H_4CO.OH.CO.OH$
Nitrobenzoic acids.............................$C_6H_4(NO_2).CO.OH$
Amidobenzoic acids............................$C_6H_4(NH_2).CO.OH$
Sulphobenzoic acids...........................$C_6H_4(SO_3H).CO.OH$
Sulphamidobenzoic acids.......................$C_6H_4(SO_2NH_2).CO.OH$

Sulphamidobenzoic anhydride (Saccharin).......$C_6H_4\begin{cases} SO_2 \\ CO \end{cases}NH$

Many of these substituted benzoic acids have received important applications and are described in detail in the sequel.

BENZOIC ACID.

Benzene-carboxylic Acid. Phenyl-formic Acid.

$C_7H_6O_2$; or, $C_6H_5.COOH$.
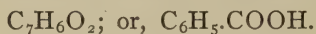
Benzoic acid occurs ready-formed in gum benzoin, storax, and Tolu and Peruvian balsams, and in these and other resins also in the form of benzoic esters. It has also been found in the perfume known as *ylang-ylang*, in vanilla, in oil of jasmine, and in certain fruits, notably plums and cranberries.

Benzoic acid is formed in numerous synthetic reactions, and is produced by the oxidation of a great number of organic bodies, including benzoic and cinnamic aldehydes, toluene, cumene, casein, gelatin, etc.

From gum benzoin the benzoic acid may be obtained by sublimation, or by exhaustion of the powdered substance with carbon disulphide. It may also be extracted from benzoin by treatment with lime in the manner indicated on page 452.[1] Benzoic acid prepared from gum-benzoin by sublimation is often more or less coloured, and has an aromatic odour.

It is prepared commercially by oxidising benzyl chloride with nitric acid.

Benzoic acid crystallises from hot water in white lustrous scales or friable needles, but its crystalline habit is greatly modified by traces of impurity, so that the impure substance has been several

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[1] The British Pharmacopœia (1898) makes no mention of benzoic acid prepared from gum-benzoin by the lime process, though much of the purest commercial acid is obtained in this manner.

times mistaken for an isomeric acid. When quite pure, benzoic acid is almost, if not quite, odourless,[1] but as met with in commerce it always has a well-marked odour, frequently smelling of benzoin, and sometimes of urine or almonds.

Benzoic acid has a sp. gr. of 1.292, melts at 121°, and boils at 249°. It volatilises readily at a temperature much below its b. p.; forming a beautiful feathery sublimate. The acid is somewhat volatile in a current of steam, and more or less with alcohol, benzene, and other volatile liquids.

Benzoic acid has a sharp taste, and produces a peculiar irritation in the throat. The vapour has a penetrating aromatic odour, attacks the eyes, and provokes coughing.

In cold water benzoic acid dissolves very sparingly, requiring 640 parts at 0°, 408 at 15° and 281 at 25°.[2] In boiling water the solubility is 1 in 17 (1 in 15, United States Pharmacopœia). Benzoic acid is dissolved very readily by alcohol, ether, chloroform, amyl alcohol, benzene, petroleum spirit, carbon disulphide, and some fixed and volatile oils.

Benzoic acid is employed in medicine and in the manufacture of colouring-matters. It possesses decided antiseptic properties, being in this respect, according to some observers, superior to salicylic acid, and, according to others, inferior.

In the report of an investigation into the effects on digestion and health, of the presence of benzoic acid or sodium benzoate in food-stuffs, H. W. Wiley (*U. S. Dept., Agric. Bureau. Chem.*, Circular No. 39, 1908) states that both these substances are highly objectionable when taken internally, the evil effects being manifested by indigestion, nausea, headache, vomiting, loss of body-weight, etc. The importance of detecting any addition of benzoic acid to foods is therefore evident.

The Referee Board appointed by the President of the United States carried out 3 independent tests during a period of 3 months and reported that benzoic acid and benzoates in moderate doses, such as

[1] 4 specimens of benzoic acid prepared by different methods and carefully purified were found by Perry to lose odour as the purification proceeded, becoming quite odourless when strictly pure. The merest trace of benzyl alcohol, benzyl benzoate, or benzaldehyde imparted a marked odour to the acid.

[2] The solubility of benzoic acid in water is much increased by the presence of certain salts, such as sodium phosphate.

SODIUM BENZENE-SULPHINATE is a compound obtained by dissolving benzoic acid in a concentrated solution of sodium sulphite. It is very soluble in water at the ordinary temperature and the solution has been recommended as an antiseptic dressing for wounds. It is said to be more efficient than phenol, and to rank with mercuric salts and iodoform, without having the poisonous characters of the former or the disagreeable odour of the latter.

would be used in foods, were harmless and that there was no cumulative effect.

Commercial Benzoic Acid.—The benzoic acid of commerce is liable to contain various impurities, some of which are due to its mode of preparation, whilst others are intentionally added as adulterants. Asbestos, boric acid, calcium carbonate and sulphate, sal-ammoniac, and sugar are among the more or less apocryphal additions of the latter class.

Pure benzoic acid does not melt in boiling water, but some impurities impart this property to it, besides giving it greater solubility, and causing it to form smaller crystals of a different form from that usually assumed by the pure acid. On treating a sample of benzoic acid with ether, nearly all impurities and adulterants are left undissolved, except cinnamic acid, chlorobenzoic acid, and essential oil.

Inorganic impurities in benzoic acid can be detected and estimated by subliming the sample, pure benzoic acid being readily and entirely volatile. If the residue chars on further heating, *sugar* or *hippuric acid* may be present. The former gives a smell resembling burnt bread, and the latter an odour of burnt feathers, and they may be readily distinguished in other ways. *Boric acid* is insoluble in ether, but dissolves in hot alcohol to form a solution which when kindled burns with a flame green at the edges. If this indication be obtained it should be confirmed by repetition on the residue left on dissolving the sample in ether, as chlorobenzoic acid might also give rise to a green-edged flame.

Hippuric acid when present may be further detected by its incomplete solubility in ether; by its charring when heated with strong sulphuric acid; and by the evolution of ammonia which occurs when the sample is ignited with soda-lime. The last test may be employed quantitatively in the absence of ammoniacal salts. The proportion of hippuric acid may be approximately estimated by agitating the sample with dilute hydrochloric acid and light petroleum or chloroform, when any hippuric (or succinic) acid remains undissolved. Samples of benzoic acid containing hippuric acid usually have a urinous odour, and redden or char when heated.

Salicylic acid may be detected by the production of a violet colouration with excess of ferric chloride. It may also be detected and estimated by treating the warm aqueous solution of the sample with bromine water which throws down the salicylic acid completely as a

white, voluminous precipitate, whilst benzoic acid gives no reaction. (Compare page 475.)

Cinnamic acid is said to be often present in considerable proportion in benzoic acid prepared from benzoin. It is best detected by its reaction with manganous salts (see page 437), and by the smell of bitter-almond oil produced on warming the sample with sulphuric acid and potassium dichromate. The presence of cinnamic acid lowers the m. p. of benzoic acid).

According to A. Jorissen (*Ann. Chim. anal.*, 1901, **6,** 41), cinnamic acid can be detected in benzoic acid in the following way: 1 grm. of the sample is dissolved in 10 c.c. of boiling water, and the solution cooled and filtered. The crystals on the filter are gently pressed to expel the mother-liquor. The latter is transferred to a test-tube, treated with 4 c.c. of a 5% aqueous solution of uranium acetate, the tube closed with a cork, and the liquid exposed to light, direct sunlight if possible. In the presence of cinnamic acid, of which 1% can be thus detected, benzaldehyde is gradually formed and can be recognised by its odour.

Chlorinated compounds are indicative of the presence of synthetic benzoic acid and should never be present in an acid prepared from natural sources. They may be detected by dissolving the sample in alcohol, moistening some asbestos with the solution, igniting it, and placing a beaker moistened with silver nitrate over the flame. If chlorinated products were present, a milky deposit of silver chloride will be produced. P. N. Raikow (*Chem. Zeit.*, 1898, **22,** 20) states that if a portion of the sample be heated on a platinum wire over a bunsen flame, and the evolved vapours allowed to come into contact with a few drops of an alcoholic solution of phloroglucinol-vanillin contained in an inverted porcelain dish held over the flame, a red colour will be developed in presence of organic chlorinated compounds.

Traces of *hydrochloric* and *sulphuric acids* are frequently present in commercial benzoic acid, owing to the method of preparation.

Sugar is recognised by its insolubility in ether, ready solubility in cold water, and by the blackening which occurs when the sample is heated with strong sulphuric acid. When present in quantity it may be detected by the taste of the sample, and in smaller quantity by the taste of the residue left undissolved by ether or chloroform.

Ammonium chloride (sal-ammoniac) is detected by shaking the sample with cold water, when a solution is obtained with which silver

nitrate gives white curdy silver chloride insoluble in nitric acid. This proves the presence of a chloride only; the presumption that ammonium chloride is present is confirmed if the sample evolves ammonia on treatment *in the cold* with alkali hydroxide. In presence of ammonium chloride and other ammoniacal salts, the soda-lime test for hippuric acid is inapplicable, unless the sample be first shaken with cold, moderately concentrated hydrochloric acid, in which ammonium chloride dissolves, whilst hippuric acid is nearly insoluble.

Essential oil, which is very commonly present in benzoic acid made from gum benzoin, causes the samples to turn brown when warmed with strong sulphuric acid. *Resinous* and *oily matters* will remain undissolved, together with any mineral matters, on treating the sample with sufficient warm dilute sodium hydroxide solution to neutralise the acid.

The odour of benzoic acid to some extent indicates its origin; but the acid from benzoin is sometimes imitated by mixing the products from other sources with benzoin, and subliming the mixture; or by adding vanillin to artificial benzoic acid. According to Hager, (*Pharm. Central*, 1886, **26,** 392), this factitious product may be detected by a mixture of solutions of ferric chloride and potassium ferricyanide. With the natural acid from benzoin, the colour of this reagent is changed from yellow to blue in from 1 to 3 seconds; whilst with the product obtained by subliming the artificial acid over resin, from 20 seconds to 2 minutes are required. The pure acid does not change the colour.

The reduction of potassium permanganate has been proposed as a test for the origin of benzoic acid, but its indications have been proved to be fallacious. Ammonio-nitrate of silver has also been recommended, the test being used at a boiling heat.

O. Jacobsen (*Arch. Pharm.*, 1884, [iii], **22,** 366) recognises the acid from gum benzoin by the presence of *catechol*, which he detects by converting the acid into a sodium salt, drying, and shaking with ether. The ether being separated and evaporated, the residue is dissolved and the catechol recognised by its reducing action on cold ammonio-nitrate of silver and by other reactions.

Jacobsen has further investigated the nature of the substances accompanying benzoic acid prepared from gum benzoin. On treating such acid with a solution of sodium carbonate, an oil remains undissolved, smelling of vanillin and of phenol. This may be separated by

distillation into 3 fractions. The first, boiling between 200° and 210°, consists of methyl benzoate and guaiacol, which can be separated by cold dilute sodium hydroxide solution. The second and smaller fraction (boiling between 235° and 245°) when shaken with water yields catechol, whilst acetyl-guaiacol remains undissolved. The third and largest fraction (boiling between 280° and 330°) contains benzyl benzoate, benzophenone, and benzoyl-guaiacol, with traces of vanillin and other substances. On saponification with alcoholic potassium hydroxide, and agitation with water and ether, benzyl alcohol and benzophenone pass into the ethereal layer, whilst the alkaline solution contains benzoic acid and guaiacol. The 2 latter substances may be separated by adding sodium hydrogen carbonate till the liquid is alkaline to litmus, and then agitating with ether, which will dissolve the guaiacol only.

Pure benzoic acid, when heated in a test-tube, sublimes completely without changing colour. It dissolves to a colourless solution in pure sulphuric acid, and if ignited with calcium carbonate, leaves a residue, the solution of which, in nitric acid, gives no opalescence with silver nitrate solution. Consequently, a sample which satisfies these 3 tests can contain no likely impurity except salicylic and sulphuric acids, which can be detected as above.

Qualitative Tests and Detection.—Strong solutions of soluble benzoates are precipitated on addition of hydrochloric acid, owing to the slight solubility of benzoic acid in water. (Succinates give no precipitate with hydrochloric acid; but hippurates, cinnamates, and salicylates react like benzoates. Sulphuric acid should not be substituted for hydrochloric acid.)

Sodium amalgam, metallic magnesium, or aluminium gradually reduce a slightly acidified solution of a benzoate, with production of the characteristic odour of benzaldehyde.

Neutral ferric chloride precipitates neutral benzoates almost completely as a light red, bulky, basic ferric benzoate, insoluble in acetic acid. Succinates give with ferric chloride a reddish-brown, cinnamates a yellow, and hippurates a cream-coloured precipitate, meconates a deep red colouration, and salicylates a violet colouration. Benzoic acid is also distinguished from succinic and many other acids by not being precipitated by ammoniacal barium chloride in presence of alcohol. Magnesium benzoate is soluble in alcohol, but the succinate is insoluble.

For the detection of benzoic acid in *foods*, E. Mohler. (*Bull. Soc. Chim.*, 1890, [iii], **3,** 414) employs the reaction of hydrogen sulphide on an ammoniacal solution of symmetrical dinitro-benzoic acid (1 : 3 : 5), whereby reduction takes place successively to amido-nitrobenzoic and diamidobenzoic acid. In the case of beer, for example, 100 c.c. are rendered alkaline by sodium hydroxide and evaporated to a paste, which is acidified with hydrochloric acid, mixed with sand, and extracted with ether (20 c.c.). The ether is evaporated, and the residue moistened with sulphuric acid (2 c.c.), heated to 240° till acid vapours are evolved and charring takes place, when a few deci-grammes of sodium nitrate are gradually added till the liquid becomes colourless. The clear liquid formed is poured into excess of aqueous ammonia and a drop of ammonium sulphide added. The least trace of benzoic acid is at once indicated by the production of a yellow coloura-tion changing to reddish-brown.

L. Robin modifies Mohler's method as follows: 50 c.c. of the liquid (beer, wine, or cider) are mixed with a little ferric chloride solution and a little hydrochloric acid, and shaken with 40–50 c.c. of ether. The ethereal extract is washed twice with water and half of it is shaken with a solution of 0.3 grm. of sodium hydrogen carbonate in a mixture of 20 c.c. of water and 5 c.c. of alcohol. The aqueous-alcoholic solution is separated, evaporated to dryness, and the residue heated with 5 c.c. of sulphuric acid and 10 drops of fuming nitric acid until sulphuric acid fumes are evolved. The acid liquid is then poured into 50 c.c. of cold water, the solution made ammoniacal and treated with a solution of ammonium hydrosulphide, drop by drop, shaking after each addition. In the presence of benzoic acid, an orange-red colouration commences to appear and develops rapidly. The addition of alkaline hydrosulphide should be arrested when the colour is first observed. It is claimed that 0.001 grm. can be detected in this way (*Ann. Chim. anal.*, 1909, **14,** 53).

For the detection of benzoic acid in butter G. Halphen (*J. Pharm. Chim.*, 1908, [vi], **28,** 201) has described a variation of Mohler's method in which the reduction is effected by sodium sulphite.

Halphen's method has been modified by Robin (*loc. cit.*) in order to avoid emulsification when the butter is extracted. 25 grm. of the butter are melted and poured into a solution of 0.5 grm. of sodium hydrogen carbonate in a mixture of 50 c.c. of water and 15 c.c. of alcohol. The mixture is stirred by giving the beaker a circular move-

ment and allowed to stand for 10 minutes. The aqueous-alcoholic liquid (which should be alkaline to litmus) is then separated, treated with 7 to 8 drops of dilute sulphuric or hydrochloric acid, heated just to boiling, treated with a little tripoli, and poured on to a moistened folded filter, large enough to contain it entirely. The filtrate (filtration must be repeated if necessary until the liquid is clear) is extracted with ether and the extract tested as already described.

J. de Brevans (*J. Pharm. Chim.*, 1909, [vi], **14,** 438), for the detection of benzoic acid or benzoates in foodstuffs, relies on the production of aniline blue when the acid is heated with aniline containing rosaniline hydrochloride. This author uses a mixture of equal parts of ether and light petroleum for the extraction. According to Halphen, the method is unsuitable for use in testing butter.

K. Fischer and O. Gruenert (*Zeitsch. Nahr. Genussm.*, 1909, **17, 721**) advocate the following method for the extraction of benzoic acid from flesh products: 50 grm. of the finely divided material are mixed with 100 c.c. of 50% alcohol, the mixture acidified with dilute sulphuric acid and stirred for 30 minutes. It is then filtered through muslin, the solid pressed, the expressed liquid made alkaline, and all the alcohol expelled by evaporation on a water-bath. When the volume has been reduced to 50 c.c., 5 grm. of sodium chloride are added, the liquid acidified with dilute sulphuric acid and heated to boiling. After cooling, the liquid is filtered, the filtrate extracted with ether, the ethereal extract washed with water and evaporated at a low temperature. For the identification of the acid in the residue, these authors prefer to convert it into salicylic acid by fusion with sodium hydroxide, the latter being recognised by the ferric chloride reaction. It is stated that de Brevans' test is useless for the detection of benzoic acid in meats and fats.

Mlle. Anna Jonescu has recently (*J. Pharm. Chim.*, 1909, [vi], **29,** 523) described a method of detecting benzoic acid by treating 1 c.c. of a solution (containing 1 grm. per litre) with 1 drop of officinal ferric chloride solution (1.28%) and 1 drop of a 0.3% hydrogen peroxide solution. The liquid, at first yellow, gradually (immediately on warming) assumes the violet colour characteristic of salicylic acid. The method, which cannot be employed in the presence of phenols, salicylic acid, or saccharin, is stated to be especially applicable to milk.

Estimation. Volumetric Methods.—Benzoic acid is distinctly acid to methyl-orange, but this indicator cannot be employed for its

titration, as the end point is very indefinite.   Benzoic acid is sharply
mono-basic towards phenolphthalein and Poirrier's blue, and may be
accurately titrated by sodium hydroxide with the aid of either of these
indicators.

The benzoic acid, liberated if necessary by acidification, is dis-
solved by repeated agitation with ether, chloroform, or benzene.
After washing the ethereal solution with water, the benzoic acid may
be estimated by adding alcohol and titrating with standard sodium
hydroxide and phenolphthalein.

Rebière (*J. Pharm. Chim.*, 1896, [vi], **3,** 113) analyses metallic ben-
zoates by carefully heating a known quantity with hydrochloric acid.
The chlorine in the resultant chloride is estimated by titration with
silver nitrate.   The method is not well-suited for the analysis of lith-
ium benzoate, owing to the ready volatility of the chloride, and is evi-
dently inapplicable to ammonium benzoate.

To estimate the benzoic acid, the salt is treated with an amount of
decinormal sulphuric acid exactly sufficient to combine with the
metallic base, the quantity of which is determined from the estimation
of chlorine in the chloride.   The liberated benzoic acid is then titrated
with standard sodium hydroxide and phenolphthalein.

As the result of a critical examination of the methods of estimating
benzoic acid in foods W. von Genersich (*Zeitsch. Nahr. Genussm.*,
1908, **16,** 224) concludes that it is most completely extracted with
benzene.   To facilitate the penetration of the solvent, it is advantage-
ous to subject fatty substances to a preliminary boiling with sodium
hydroxide solution.   One or two drops of phenolphthalein solution are
added to an aliquot part of the benzene extract and the liquid titrated
with $N/10$ potassium hydroxide solution.   (1 c.c. corresponds to
0.0122 grm. of benzoic acid.)

Gravimetric Methods.—Benzoic acid may be *separated* from fixed
substances by sublimation, and may be estimated in gum benzoin
by that means.

Benzoic acid may also be approximately estimated, in the absence
of interfering substances, by converting it into a soluble neutral ben-
zoate, and precipitating the cold solution with lead acetate, avoiding
excess.   The precipitate is filtered off, washed once with cold water,
then with proof-spirit containing 0.5% of acetic acid, and finally dried
at 100° and weighed.   Its weight, multiplied by 0.5432 gives the amount
of benzoic acid present.

Neutral benzoates are precipitated tolerably perfectly by cupric acetate or sulphate, especially in presence of alcohol, and the action may be employed for the estimation of benzoic acid.

After extracting the benzoic acid from its acidified solution with ether, sodium hydroxide or baryta may be added to the ethereal layer with constant agitation until the liquid is exactly neutral (to phenolphthalein). The ethereal layer (which will retain any benzaldehyde or essential oils) is separated and the aqueous liquid evaporated to dryness, the residue dried at 100°, and the benzoate weighed.

F. M. Horn (*Zeit. Chem. Ind.*, 1888, **2**, 329) recommends the following method of estimating benzoic acid in milk: About 10 c.c. diluted with an equal volume of water are warmed with dilute hydrochloric acid (1%) until it coagulates. After filtering and washing the precipitate with warm water, the filtrate is evaporated and the residue taken up in 50% alcohol. A few drops of ammonia are added to this solution after filtration, the excess boiled off, and the liquid exactly neutralised and treated with its own volume of absolute alcohol. The benzoic acid is precipitated with copper sulphate and weighed on a tared filter as copper benzoate.

For the estimation of benzoic acid in catsup La Wall and Bradshaw (*Amer. J. Pharm.*, 1908, **80**, 171) recommend the following method: 20 grm. of the sample are mixed with 5 c.c. of hydrochloric acid and 25 c.c. of a saturated solution of sodium chloride, the mixture shaken for 5 minutes and poured on to a moistened filter. The residue on the filter is washed with saturated salt solution until the filtrate and washings amount to 100 c.c. The latter is shaken 3 times with chloroform, and the united extracts evaporated at ordinary temperature. The residue is dried to constant weight over sulphuric acid. It is usually white and crystalline, but if yellow and oily, it should be dissolved in ammonia, the solution acidified with sulphuric acid and the extraction with chloroform repeated. The estimation may be confirmed volumetrically by dissolving the weighed residue in a little alcohol and titrating with $N/20$ potassium hydroxide solution, using phenolphthalein as indicator. After titration it is advisable to divide the neutral solution into 2 parts, 1 of which is tested for cinnamic acid by adding manganous sulphate solution, and the other for salicylic acid by adding excess of ferric chloride solution. Saccharin and salicylic acid if present in the catsup are extracted with the benzoic acid and must be

estimated separately, and the quantities found deducted from the total weight of the residue.

Another method of estimating benzoic acid in catsup is described by Reed (*J. Amer. Chem. Soc.*, 1907, **29**, 1626), but this is a lengthy process and requires a flask of a special pattern.

METALLIC BENZOATES.

The metallic benzoates are mostly crystallisable and soluble in water and alcohol, but insoluble in ether. Some of them, such as the sodium and barium salts, are withdrawn from their solutions by animal charcoal, and calcium benzoate is decomposed by it, so that free benzoic acid can be extracted by treating the charcoal with ether.

The general reactions and methods of analysing metallic benzoates have already been described above.

Commercial benzoates are liable to contain much the same impurities as benzoic acid (page 406), especially *hippuric* and *chlorobenzoic acids, sulphates,* and *chlorides.* The 2 former impurities may be detected by acidifying the solution of the benzoate with hydrochloric acid and agitating with ether. Benzoic and chlorobenzoic acids pass into the ethereal layer, whilst hippuric acid remains (undissolved) in the aqueous liquid. The chlorobenzoic acid or other organic chlorine compounds may then be detected by allowing the bulk of the ether to evaporate spontaneously, adding alcohol, igniting, and testing the products of combustion for hydrochloric acid, as described above.

Sodium benzoate, $NaC_7H_5O_2 + H_2O$, crystallises in colourless needles. The salt is soluble in 1.7 parts of water at 15° if the acid used for its preparation were pure, but has a lower and varying solubility if chlorobenzoate or hippurate be present. Sodium benzoate receives an extensive application in America in the preservation of articles of food (see page 405).

Potassium benzoate, $KC_7H_5O_2 + 3H_2O$, forms concentrically grouped needles.

Lithium benzoate forms a crystalline powder or small shining scales, soluble in 4 parts of cold or 25 of boiling water and in 12 parts of cold or 10 of boiling alcohol. It is liable to contain the same impurities as sodium benzoate (see above) and lithium citrate (Vol. i).

Calcium benzoate, $Ca(C_7H_5O_2)_2 + 3H_2O$, crystallises in granules or feathery needles, and is less soluble in hot water than in cold.

Manganous benzoate is soluble in water (distinction from cinnamate).

Ferric benzoate is obtained as a flesh-red precipitate by mixing solutions of neutral benzoates and ferric chloride. It is decomposed by washing with water into a soluble acid and an insoluble basic salt.

Cupric benzoate, $Cu(C_7H_5O_2)_2 + 2H_2O$, crystallises from hot water in light blue needles or plates united in spherical masses. It is one of the least soluble of the benzoates.

Lead benzoate is crystalline and difficultly soluble.

Mercuric benzoate, $Hg(C_7H_5O_2)_2$, forms long silky crystals soluble in hot water, but very sparingly soluble in cold water. It is more readily dissolved by water containing chlorides or iodides. According to Rebière (*Pharm. Jour.*, 1887, **1,** 82), mercuric benzoate as met with in commerce is of very variable composition, as exemplified by the following analyses:

	A	B	C	D	Theory
Mercury	54.78	52.80	42.60	45.12	45.25
$C_7H_5O_2$	24.80	23.20	58.00	54.75	54.75
HCl	16.79	traces	traces	....	....
HNO_3	traces	20.36	traces	....	....

The salt can be obtained of almost theoretical composition (as was sample D) by precipitating mercuric chloride with excess of sodium hydroxide, washing the mercuric oxide till free from chlorine, and boiling it with the calculated quantity of powdered benzoic acid in a little water, leaving the oxide in slight excess. On boiling the resulting powder with a large quantity of water it dissolves, and on cooling pure mercuric benzoate crystallises out.

Bismuth Benzoate.—A basic salt, stated to have the composition $BiO . C_7H_5O_2$, is official in France. It is prepared by treating benzoic acid with freshly prepared moist bismuth hydroxide. The salt is amorphous, and commercial samples show somewhat varying composition.

BENZOIC ESTERS.

Benzoic esters are obtained by the general methods used to prepare this class of compounds.

Methyl benzoate, $C_6H_5 . CO_2Me$, an aromatic liquid boiling at

199°, is used to a limited extent in the preparation of artificial fruit essences and flavourings.

Ethyl benzoate, $C_6H_5.CO_2Et$, is a very fragrant liquid, boiling at 213°. It is employed in the production of artificial fruit essences (see Vol. i), but is valueless in perfumery.

Propyl benzoate boils at 229°, and *butyl benzoate* at 247°.

Benzyl benzoate, $C_6H_5.CO_2C_7H_7$, is a natural constituent of Peru and Tolu balsams. It forms compact lustrous crystals of aromatic odour, melts at 20° to 21°, and boils at 323°. At its m. p. it has a sp. gr. of 1.227.

The so-called "cinnamein" of Peru balsam consists of a mixture of benzyl benzoate and cinnamate, in which the former constituent largely predominates. Benzyl benzoate is the constituent to which the efficacy of Peru balsam in the treatment of scabies is due. The synthetic ester has the advantage of being of constant composition and free from colour and odour, whilst it does not cause the irritation, due to the presence of free acid, which is sometimes a consequence of using Peru balsam. Benzyl benzoate has been introduced into commerce by the Berlin Aniline Company under the name of "*Peruscabin.*" A 25% solution of the ester in castor oil is known as "*Peruol.*"

Eugenyl benzoate, $C_{10}H_{11}O.C_7H_5O_2$, prepared by heating together eugenol and benzoyl chloride, forms the "*Benzeugenol*" of medicine. It has been employed as an antiseptic in cases of tuberculosis. It forms colourless, odourless, bitter crystals, very slightly soluble in water, but easily soluble in hot alcohol, ether, chloroform, and acetone. Benzeugenol melts at 70.5°, and gives a purple colouration with strong sulphuric acid. The formation of eugenyl benzoate is the basis of Thoms' method for the estimation of eugenol in essential oils.

Guaiacyl benzoate, or benzoyl-guaiacol, $C_6H_4(OCH_3).O.-CO(C_6H_5)$, also called "*Benzosol,*" is recommended as a useful substitute for guaiacol in phthisis. It has the advantage over the latter of being tasteless and odourless. Benzosol forms small colourless crystals, melting at 57°. It is almost insoluble in water, but is readily soluble in hot alcohol, ether, and chloroform.

According to Dragendorff (*Arch. Pharm.*, 1895, **233**, 612) benzoyl-guaiacol gives a reddish-purple colour when moistened with sulphuric acid and acetone; a violet colour striped with green and violet-blue, with ferric chloride; an orange and green colour with nitric acid; a

green, violet, and yellow colour with potassium nitrite; a bright red colour with sucrose or dextrose; a violet to red colour with Fröhde's reagent; and a violet, green, and blue colour with sulphovanadic acid.

Benzoic Anhydride. Benzoyl Oxide. $\begin{array}{c} C_6H_5.CO \\ C_6H_5.CO \end{array}\Big\rangle O$

This substance is prepared according to methods described by Gerhardt (*Annalen*, 1853, **87**, 73), Lachowicz (*Ber.*, 1884, **17**, 1282) and Minunni (*Gazzetta*, 1890, **20**, 655; 1892, **22**, ii, 213).

Benzoic anhydride crystallises in rhombic prisms melting at 42°. It boils at 360°, and dissolves readily in alcohol or ether. It is but little affected by cold water, but on boiling with water readily undergoes hydrolysis with formation of benzoic acid. By boiling with alcohol it yields *ethyl benzoate*. This and similar reactions render benzoic anhydride a valuable reagent for the production of benzoic esters, and it is employed for that purpose in the investigation of essential oils.

Benzoyl Chloride. Benzoic Chloride. $C_6H_5.COCl.$

Benzoyl chloride may be prepared by the action of phosphoric chloride on benzoic acid (Cahours, *Annalen*, 1849, **70**, 40), or by the action of chlorine on benzaldehyde. It is a liquid of penetrating odour. It boils at 198°, and solidifies at a low temperature, the solid melting at —1°. It is isomeric with the *chlorobenzaldehydes*, $C_6H_4Cl.CHO$, and is a valuable reagent in organic synthesis.

Commercial benzoyl chloride is usually contaminated with chlorobenzoic chloride, and frequently with benzaldehyde and its chloroderivatives. These impurities cause synthetic compounds prepared with it to contain chlorine compounds difficult to remove.

Benzoic Aldehyde. Benzaldehyde.

$$C_7H_6O; \; i. \; e., \; C_6H_5.CHO.$$
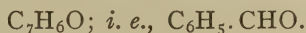
Benzaldehyde forms the major part of the essential oils of bitter almond, cherry-laurel, peach kernels, and many other vegetable products, especially of members of the natural order *Rosaceæ*.

It is manufactured synthetically chiefly by the action of lead or copper nitrate on benzoyl chloride. (Compare Lauth and Grimaux, *Bull. Soc. Chim.*, 1867, [i], **7**, 106; Piria, *Annalen*, 1856, **100**, 105; and Anschütz, *Annalen*, 1884, **226**, 18.)

Pure benzaldehyde is a thin colourless liquid of high refractive power. It has a peculiar, very agreeable odour like that of bitter-almond oil, and a burning aromatic taste. Its sp. gr. is 1.0636 at 0° and 1.0504 at 15°. It solidifies at —13.5° and boils at 179°. Benzaldehyde is soluble in about 300 parts of water, and is miscible in all proportions with alcohol and ether.[1]

Synthetic benzaldehyde is largely used, for flavouring and perfumery purposes, as a cheap substitute for the natural essential oil of almonds. Most of the synthetic benzaldehyde of commerce contains traces of chlorinated compounds, which are particularly objectionable, since they have an irritating odour, and cause soaps perfumed with the impure substance to deteriorate and darken on exposure to light. Benzaldehyde can, however, be obtained quite free from such impurities, and soap scented with it does not change colour on exposure. As a perfume, artificial benzaldehyde is inferior to the natural oil of almonds.

Benzaldehyde is employed largely for the production of various synthetic products, such as malachite-green, cinnamic aldehyde, etc.

Reactions.—On exposure to the light, benzaldehyde absorbs oxygen rapidly, and is converted into a crystalline mass of benzoic acid, $C_7H_6O_2$.[2] (Cf. Baeyer and Villiger, *Ber.*, 1900, **33,** 1569.) It is also oxidised by boiling with chromic acid mixture, or manganese dioxide and sulphuric acid; but is only slowly attacked by nitric acid, even when boiling.

When heated with solid sodium hydroxide, benzaldehyde evolves hydrogen and yields a benzoate. By treatment with water and sodium amalgam, it is reduced to benzyl alcohol. Benzyl alcohol and a benzoate are also formed when benzaldehyde is treated with strong sodium hydroxide solution.

Like most aldehydes, benzaldehyde forms crystalline compounds with alkali hydrogen sulphites. The sodium compound has the formula C_7H_6O . $NaHSO_3$.[3] Benzaldehyde also responds to the other general reactions of aromatic aldehydes. It reduces ammoniacal silver solution with the production of the usual silver mirror, but differs from aldehydes of the aliphatic series in being permanent in

[1] The solubility of benzaldehyde in water is often erroneously stated as 1 in 30, which is 10 times the true amount.

[2] The oxidation is much retarded by the presence of hydrocyanic acid, which is therefore often added to the artificial oil of bitter almonds.

[3] This insoluble crystalline compound is converted, in the presence of an excess of sodium hydrogen sulphite, into a soluble compound of the formula $C_7H_5NaSO_3$.

presence of alkalies and in not reducing Fehling's solution. Ammonium hydroxide converts benzaldehyde into white crystalline *hydrobenzamide*, $(C_6H_5.CH)_3N_2$, melting at 110°, which is resolved by acids into ammonia and benzaldehyde. This reaction also distinguishes the aromatic aldehydes from those of the fatty series.

Estimation. Volumetric Methods.—Ripper has devised a general method for the estimation of aldehydes and those ketones which combine with sodium hydrogen sulphite (*Monatsh.*, 1901, **21,** 1079). The aldehyde or ketone is absorbed (after steam distillation if necessary) in excess of sodium hydrogen sulphite solution and the excess determined by titration with standard iodine solution. In the experience of the present writer, however, the excess of sulphite found after the absorption of benzaldehyde, varies with the concentration of the solution, and consequently appreciable errors are introduced by variation of the duration of the steam distillation, when this is necessary.

Gravimetric Methods.—For the estimation of small quantities of benzaldehyde Hèrissey (*J. Pharm. Chim.*, 1906, [vi], **23,** 60) converts the aldehyde into its phenylhydrazone. The reaction is not complete at the ordinary temperature in 24 hours, and longer periods give too high results owing to oxidation of the excess of phenylhydrazine. The following method, however, is stated to give good results: 50 c.c. of the aqueous solution of benzaldehyde are mixed with 50 c.c. of a reagent prepared by dissolving 0.5 c.c. of acetic acid and 1 c.c. of freshly distilled phenylhydrazine in 100 c.c. of water. The mixture is heated on a water-bath for 20 to 30 minutes and then allowed to stand for 12 hours. The precipitate is collected in a tared Gooch crucible, washed with 20 c.c. of cold water, and dried to constant weight over sulphuric acid *in vacuo*. Denis and Dunbar (*J. Ind. Eng. Chem.*, 1909, **1,** 256) employ a similar method for the analysis of almond-flavouring extracts, but as they allow the mixture of extract and phenyl hydrazine to stand 24 hours without heating, their results are somewhat low.

Colourimetric Method.—Woodman and Lyford have based a method of estimating benzaldehyde in almond extracts on the colour reaction of aldehydes with magenta decolourised by sulphur dioxide. (*J. Amer. Chem. Soc.*, 1908, **30,** 1607.)

This has the advantage of being considerably more rapid than the gravimetric method. The reagent is prepared by dissolving 0.5 grm. of magenta in 100 c.c. of water, adding a solution of 20 grm. of sul-

phur dioxide and diluting to 1 litre. 3 standard solutions are prepared by dissolving, respectively, 0.002 grm., 0.004 grm., and 0.006 grm. of freshly distilled benzaldehyde in aldehyde-free alcohol and diluting to 20 c.c. 10 grm. of the sample to be analysed are diluted to 50 c.c. with alcohol (aldehyde-free), and of this solution 2 c.c. are diluted to 20 c.c. with the same solvent. The latter solution and the 3 standards, contained in Nessler tubes, are immersed for some time in water at 15°, then each is treated rapidly with 20 c.c. of the magenta reagent (also at 15°) and well mixed. After standing for 10 minutes the test sample is matched with the nearest standard in the usual way by withdrawing part of either liquid. The depth of colour, within the given limits, is proportional to the amount of benzaldehyde present. To prepare aldehyde-free alcohol it is distilled over silver oxide, then treated with 25 grm. of *m*-phenylene-diamine hydrochloride per litre, and a rapid current of air passed through the solution for 3 hours. The liquid is then distilled, the first 100 c.c. being rejected. Alcohol so treated remains pure for some weeks if kept in the dark at a low temperature.

ESSENTIAL OIL OF BITTER ALMONDS.

The essential oil of bitter almonds, *Amygdalus communis* var. *amara*, together with the oils of several other kernels, such as those of the apricot and peach, owe their characteristic odour and flavour to benzaldehyde.[1] To all intents and purposes the oils from these 3 sources are identical, and most of the foreign bitter-almond oil is in reality peach-kernel oil.

Lewkowitsch states (*Analyst*, 1904, **29,** 105) that the oil sold as "Oil of sweet almonds, French" is solely peach-kernel or apricot-kernel oil, whilst "Almond-oil, English" is genuine.

The oil does not exist in the free state in the kernels, but results from the decomposition of a glucoside, *amygdalin*, $C_{20}H_{27}NO_{11}$, which breaks down in the presence of water under the influence of the natural enzyme *emulsin* or *synaptase* into a mixture of dextrose, benzaldehyde and hydrocyanic acid.

This reaction is also brought about by the action of dilute hydrochloric acid.

[1] According to Tilden, cherry-laurel oil consists of benzaldehyde, less than 2% of hydrocyanic acid, a volatile oil (possibly benzyl alcohol), convertible into benzoic acid by oxidation, and minute quantities of an odorous resin (*Pharm. J.*, 1875, (iii), **5,** 761).

Pure oil of bitter almonds contains much hydrocyanic acid (*vide infra*), but the acid-free oil is a regular commercial article, sold as "Oil of Almonds, S. A. P." (*sine acido prussico*).

Approximately from 1 to 2% of essential oil is obtained from the bitter-almond kernels, and this possesses a much finer and more delicate odour than synthetic benzaldehyde. Bitter-almond oil is a yellowish liquid (which can be obtained colourless by rectification) of sp. gr. 1.045 to 1.070. The latter gravity is, however, somewhat rare, and normal oils seldom range outside the limits 1.045 and 1.060.

M. Boyveau states that an artificial oil of bitter almonds is occasionally met with having a sp. gr. of 1.029 to 1.030. Its odour is more acrid than that of the natural oil, as may be observed by moistening strips of paper with the oil and exposing them to the air.

Oil of bitter almonds is optically inactive, and neutral to ordinary indicators when fresh. On exposure to light it rapidly absorbs oxygen and deposits crystals of benzoic acid, at the same time becoming acid in reaction.

The main constituent of essential oil of bitter almonds is benzaldehyde, but a notable proportion of hydrocyanic acid (4 to 8%) is present, and appreciable quantities of phenyl-hydroxyacetonitrile (the nitrile of mandelic acid), $C_6H_5.CH(OH).CN$.[1] This last-named substance, also known as benzaldehyde-cyanohydrin, is formed by a direct combination of benzaldehyde and hydrocyanic acid.

Mandelo-nitrile has a sp. gr. of 1.124, and is easily decomposable. Hence normal almond oils containing from 1.5 to 4% of hydrocyanic acid have a sp. gr. usually falling between the limits of 1.052 and 1.058. Oils containing a larger quantity of hydrocyanic acid, even up to 11%, have been known to reach the very abnormal sp. gr. of 1.096.[2]

When oil of bitter almonds is fractionally distilled, hydrocyanic acid passes over first, and then tolerably pure benzaldehyde.

Oil of bitter almonds may be deprived of its hydrocyanic acid in several ways. Treatment with water, mercuric oxide, lime, and

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[1] BENZOIN, $C_6H_5.CH(OH).CO.C_6H_5$, is stated to be present in some specimens of bitter-almond oil. It is a solid camphor-like substance melting at 137°, and occurs most largely in samples of oil of high density, in the preparation or purification of which a high temperature has been employed. It gives a purple colour with strong sulphuric acid.

[2] Schimmel & Co., (*Report*, April, 1893) added a 20% solution of hydrocyanic acid to a sample of bitter-almond oil which had a sp. gr. of 1.054. In two days the sp. gr. had risen to 1.074. It is thus clear that bitter-almond oils of high gravity contain comparatively large proportions of mandelo-nitrile.

ferrous chloride has been recommended. Mackay treats the oil for 48 hours with lime and solution of potassium hydroxide.

Bitter-almond oil is stated to give a crimson colouration with strong sulphuric acid, becoming brownish on exposure to the air. If the crimson liquid be poured into water the red colour disappears, and a yellow precipitate is produced, which sometimes takes the form of globules.

Essential oil of peach kernels is frequently sold as oil of bitter almonds, but the most common falsification is synthetic benzaldehyde.

Chwolles states (*Chem. Zeit.*, 1903, **27**, 33) that the phloroglucinol reaction of peach-kernel oil, described by Kreis (*Chem. Zeit.*, 1902. **26**, 897, 1014) is not given by almond oil. But Lewkowitsch (*loc. cit.*) records the occurrence of genuine almond oils which do not differ from peach-kernel oil in this respect. According to this author, the only test which will differentiate almond oil from apricot-kernel and peach-kernel oils is Bieber's test. In this 5 c.c. of the oil are treated with 1 c.c. of a mixture of equal weights of sulphuric and fuming nitric acids. Peach-kernel oil gives a peach-blossom tint, apricot-kernel oil gives a pink colour, whilst almond oil remains colourless. Admixture of 33% of apricot-kernel oil can be recognised by this means. The reaction is not so marked when the oils have been kept, and the nitro-sulphuric reagent must be fresh.

To distinguish the natural from the artificial product, Boyveau shakes 1 c.c. of the oil with 1 c.c. of concentrated sulphuric acid. The *natural oil* becomes currant-red, deepening in a few hours to a more intense and darker red, the mixture remaining perfectly clear. *Cherry-laurel* immediately takes a dark red tint, without first passing through the delicate currant-red shade observed with bitter-almond oil. The mixture thickens somewhat, but remains perfectly fluid and clear. The oils from *peach*, and *apricot-kernels* behave somewhat similarly, but give an evanescent currant-red tint, changing to a very dark red. *Artificial almond oil* first takes a red tint, and then immediately becomes brown, loses its transparency, and thickens, becoming a solid brownish mass in the course of 24 hours. By the loss of transparency and production of the brown colour an admixture of 25% of the artificial oil in the natural oil of bitter almonds is said to be recognisable.

Synthetic benzaldehyde, as already stated, usually contains marked traces of organic chlorine compounds. Some commercial specimens are free from these impurities and command a far higher price.

The U. S. Pharmacopœia, 8th Rev., has adopted a method of S. S. Sadtler. The method is as follows:

Assay of Benzaldehyde.

Into a tared 150 c.c. flask, 10 c.c. of purified kerosene are introduced, the weight noted, 12 drops of the almond oil added, and the weight again determined. To the solution 20 c.c. of water and 6 drops of phenolphthalein solution (1% in 50% alcohol) are added, and the liquid exactly neutralised with N/10 sodium hydroxide, the flask being thoroughly shaken. A 20% solution of sodium sulphite is gradually added from a burette, alternately with N/2 hydrochloric acid, from a second burette, until 10 c.c. of the sodium sulphite solution have been added, and sufficient N/2 hydrochloric acid to maintain the mixture neutral. After addition of a few drops of phenolphthalein solution and frequent agitation of the flask, it is allowed to stand for 2 hours to insure a condition of permanent neutrality, and then the volume of standard acid used is noted. A blank experiment is made, and the number of c.c. of acid required is deducted from that necessary in the actual estimation. Each 1 c.c. of difference corresponds to 0.0526 grm. of benzaldehyde.

Lunge (*Chemische-Technische Untersuchungs Methoden*, Vol. 3, pagel 807 [1905]) recommends the following methods for detecting benzyl chloride and chlorobenzaldehyde.

Benzyl Chloride.—10 grm. of the sample are distilled and the first 10 to 12 drops of the distillate collected in alcoholic potassium hydroxide solution (5%). This solution is boiled for some time in a reflux apparatus and then evaporated to dryness. The residue is dissolved in water, any oil remaining extracted with ether, and the aqueous solution treated with nitric acid. The precipitated benzoic acid is filtered off, and the filtrate tested with silver nitrate.

Chlorobenzaldehyde.—2 c.c. of the oil are shaken with a solution of 6 grm. of sodium carbonate in 40 c.c. of water, the liquid gently warmed and treated gradually with a 5% solution of potassium permanganate until a faint pink tint is permanently formed. The excess of permanganate is then destroyed by addition of alcohol drop by drop. The liquid is filtered, acidified with dilute sulphuric acid, well cooled and the precipitated benzoic acid collected. This is washed with cold water, dissolved in sodium carbonate solution containing potassium

nitrate, and the liquid evaporated to dryness. The residue after ignition is dissolved in dilute nitric acid and tested with silver nitrate solution. The occurrence of organic chlorine compounds in oil of bitter almonds may be regarded as very strong evidence of adulteration with synthetic benzaldehyde.

Hydrocyanic acid may be detected in bitter-almond oil by agitating the sample with water, and applying tests to the latter. Ferric chloride and ferrous chloride or sulphate should be added, and then a solution of sodium hydroxide. On acidifying the liquid with hydrochloric acid, a bluish-green colouration or prussian-blue precipitate will be formed if hydrocyanic acid was present. An aliquot part of the aqueous solution may be employed for quantitative estimation by precipitation or titration with silver nitrate.

A preferable method is to dissolve 1 grm. of the oil in 5 c.c. of alcohol and dilute with water to 50 c.c. Excess of ammonio-silver nitrate is then added, and the mixture well agitated for a few minutes. The solution is then slightly acidified with nitric acid, and the precipitated silver cyanide collected, washed, dried, and weighed, or ignited in the air and the resultant metallic silver weighed. 5 parts (nearly) of silver cyanide or 4 of metallic silver correspond to one of hydrocyanic acid.

Occasionally *alcohol* is added, but this is not always done with a fraudulent intention, as it is believed to retard oxidation.

Alcohol reduces the density of bitter-almond oil.

According to Lunge, it is best detected by shaking the oil in a graduated cylinder with an equal volume of a saturated solution of calcium chloride. The presence of alcohol and approximately its amount will be indicated by a decrease in volume of the oil.

Nitrobenzene, $C_6H_5NO_2$, is sometimes used as an adulterant of bitter-almond oil, and has even been sold as a substitute under the name of "artificial essence of bitter almonds." Nitrobenzene has a density of 1.186, and hence is heavier than bitter-almond oil, from which it also differs in not yielding benzoic acid when a current of air is passed through it. It is an insidious poison, and should be rigidly excluded from articles of food.

The following method may be employed for the detection and approximate estimation of nitrobenzene in bitter-almond oil. Some clean sand or emery is introduced into a wide-mouthed flask, and a known weight (about 10 grm.) of the sample to be tested, added.

This is followed by 40 c.c. of a saturated aqueous solution of sodium hydrogen sulphite, the whole agitated briskly for a few minutes, and then shaken with ether free from alcohol. The benzaldehyde forms a compound with the sulphite, whilst any nitrobenzene dissolves in the ether. The upper layer is withdrawn by a pipette, more ether added, and the agitation repeated. The ether is again withdrawn by means of the pipette, the united ethereal liquids evaporated at a gentle heat, and the residual nitrobenzene weighed. The method is only roughly approximate. If the quantity of nitrobenzene be small or there be any doubt as to its identity, 4 or 5 drops of the sample should be dissolved in alcohol and heated for some time with hydrochloric acid and granulated zinc. The nascent hydrogen reduces the nitrobenzene to aniline, C_6H_7N. The liquid is filtered through wet paper, rendered alkaline with a solution of sodium hydroxide,[1] agitated with ether, and the ethereal layer removed and shaken with water and a few drops of dilute hydrochloric acid. The ether is separated, and a dilute solution of bleaching powder is cautiously added to the aqueous liquid, when if nitrobenzene were originally present, a violet colour (mauve) will be developed. The process requires to be skilfully conducted. Reduction to aniline may be conveniently used for distinguishing bitter-almond oil from nitrobenzene, but not for detecting the latter in presence of the former. When this is required, the sulphite and ether process must be previously used for their separation.[2]

The following method for detecting and approximately estimating nitrobenzene in bitter-almond oil is due to Maisch. 1 c.c. of the sample is dissolved in 12 c.c. of absolute alcohol, and 0.75 grm. of fused potassium hydroxide added. The liquid is boiled till it is reduced to about 4 c.c., and left to cool. If the sample be pure no crystals form, but a brown colour is slowly developed. The residual liquid is entirely soluble in water. In the presence of nitrobenzene, brown crystals of azo-oxybenzene, $C_{12}H_{10}N_2O$, are formed, which are insoluble in water, and may be collected, dried by pressure, and weighed.

Mapurgo (*Pharm. Zeit. Russ.*, 1890, **29**, 205) detects nitrobenzene by the following test: 2 drops of phenol, 3 drops of water, and a fragment of potassium hydroxide the size of a pea are heated to

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[1] When the nitrobenzene occurs in quantity, bleaching powder may be added at once to the filtered liquid after nearly neutralising it with alkali.
[2] Most other essential oils can also be separated from benzaldehyde by means of sodium-hydrogen sulphite and ether.

boiling in a small basin, added to a little of the oil mixed with water, and the mixture boiled. The formation, at the conclusion of the heating, of a crimson-red ring at the surface of the liquid changed to emerald-green by adding calcium chloride solution indicates the presence of nitrobenzene.

Benzoic acid is always present, 1 to 3% being not unusual in the best commercial products. It may be estimated by dissolving 10 grm. of the oil in 50 c.c. of alcohol and titrating the solution with N-sodium hydroxide solution, using phenolphthalein as indicator.

According to the United States Pharmacopœia, oil of bitter almonds must contain 85% of benzaldehyde and not more than 4% nor less than 2% of hydrocyanic acid.

Essence of bitter almonds is the name given to a solution of commercial oil of bitter almonds in different proportions of rectified spirit. It is employed as a flavouring agent, for which purpose it should be quite free from hydrocyanic acid. *Almond flavour* is a solution of one part of the oil in 7 of rectified spirit. The proportion of alcohol in these preparations is best estimated by fractional distillation.

Bitter-almond water is a solution of bitter-almond oil in water.

Fromm states (*A poth. Zeit.*, 1897, **12,** 254) that artificial bitter-almond water consists of hydrocyanic acid, benzaldehyde, mandelonitrile, water, and alcohol, whilst the natural product contains in addition small quantities of ammonia and of substances having a peculiar odour, possibly amido-compounds. To distinguish the artificial from the natural product, 10 c.c. are treated with 20 c.c. of hydrogen peroxide solution (free from hydrogen chloride), then warmed with 2 to 5 grm. of sodium hydroxide until the odour of benzaldehyde disappears, and evaporated to dryness. The residue is gently ignited, dissolved in nitric acid and the solution tested with silver nitrate. Chlorine is present in the artificial, but not in the natural substance. It is not a preparation of the British Pharmacopœia, but is official in several other countries. Its strength is uncertain. The proportion of hydrocyanic acid it contains may be estimated with silver nitrate after adding sufficient magnesium hydroxide to leave the sample slightly opalescent. The mixture should be left at rest for half an hour and then titrated with decinormal silver nitrate, using neutral potassium chromate as an indicator. Basic magnesium acetate is said to be preferable to magnesium hydroxide (Beckurts, *Pharm.*

Central., 1887, **8**, 131; Linde, *Arch. Pharm.*, 1887, [iii], **25**, 690). Bitter-almond water should retain its characteristic odour after the removal of all the hydrocyanic acid by the above process or by agitation with excess of silver nitrate.

To test for excess of hydrocyanic acid in bitter-almond water, 10 c.c. should be treated with 1 c.c. of decinormal silver nitrate and a few drops of nitric acid, and filtered. The filtrate should give no immediate precipitate on addition of more silver nitrate.

Cherry-laurel water (*Aqua lauro-cerasi*, British Pharmacopœia), prepared by distilling fresh cherry-laurel leaves with water, and **Cherry water,** from wild cherries, are preparations very similar to bitter-almond water; but the last-named becomes milky immediately on addition of ammonia, which is an effect not produced on laurel water till after the lapse of some time.

The British Pharmacopœia requires cherry-laurel water to contain 0.10% of HCN, when assayed by titration with standard silver nitrate solution.

Acetophenone.   Phenyl-methylketone, $C_6H_5.CO.CH_3$.

This substance results from the action of benzoyl chloride on zinc-methyl or by distilling a mixture of calcium benzoate and acetate (Friedel, *J.*, 1857, 270). It may also be readily prepared by the interaction of benzene and acetyl chloride in the presence of aluminium chloride (Friedel and Crafts, *Ann. Chim. Phys.*, 1886, [vi], **1**, 507). The 2 last-named methods are those usually adopted on the manufacturing scale.

Acetophenone crystallises in large laminæ, melting at 20° to a colourless, mobile liquid of about the density of water, boiling at 202°. It has a very persistent odour, recalling that of bitter-almond and cherry-laurel water. It is nearly insoluble in water, soluble in 60 parts of glycerol and very soluble in alcohol, ether, chloroform, light petroleum, and fatty oils. Dissolved in fixed oil of almonds, it is frequently administered in gelatin capsules.

Reactions.—Acetophenone is neutral and gives no colouration or characteristic reaction with ferric chloride, hydrochloric acid, or sulphuric acid. By oxidation with chromic acid mixture it is converted into benzoic and carbonic acids. With nitric acid it gives a yellow colouration.

Acetophenone has hypnotic properties, and has been introduced into medicine under the name of "hypnone" (*Pharm. J.*, 1886, [iii], **16**, 445, 582).

Estimation.—According to Marsh and Struthers (*Proc.*, 1908, **24**, 267), acetophenone reacts with mercuric iodide, dissolved in cold aqueous potassium hydroxide, as shown by the equation

$$PhCOMe + 6HgI_2 + 4KOH = HgI, PhCO.CHg_3I_3 + 2K_2HgI_4 + 4H_2O$$

the ketone compound being a yellow precipitate. In the absence of other ketones, therefore, acetophenone may be estimated either by determining volumetrically the amount of alkali absorbed in the presence of excess of mercuric iodide, or by weighing the precipitate formed.

Gallacetophenone. $CH_3.CO.C_6H_2(OH)_3$. This substance, also known as *trihydroxyacetophenone* and as "Alizarin Yellow C," may be regarded as a trihydroxy derivative of acetophenone or as a methylketo-compound of pyrogallic acid. It is a yellow powder, melting at 168°, and is soluble in warm water, alcohol, ether, and glycerol. It is only very slightly soluble in cold water, but more so in solution of sodium acetate. It is used (in the form of an ointment) to a certain extent as a remedy for psoriasis, being a substitute for pyrogallol.

$$\textbf{Saccharin:} \quad C_6H_4 \Big\langle {}^{CO}_{SO_2} \Big\rangle NH.$$

1-2-sulphaminbenzoic anhydride; o-benzoicsulphinide; Benzosulphinidum (United States Pharmacopœia, viii); *Glusidum* (British Pharmacopœia).

Saccharin is prepared by sulphonating toluene, converting the mixed sulphonic acids into the sulphochlorides, separating the *o*-isomeride, converting this into the amide, and oxidising the latter with potassium permanganate. (Fahlberg and Remsen, *Ber.*, 1879, **12**, 469; Fahlberg and List, *Ber.*, 1887, **20**, 1597; von Heyden, D. R. P. 85491; Bayer & Co., D. R. P. 96125.)

The crude material is often contaminated with by-products, among which is 1-4-sulphaminobenzoic acid. Numerous methods for the purification of the saccharin have been proposed, among which are the following:

A. R. Ling (*Br. pat.*, 1893, 21417) proposes treatment of the crude product with a solution of sodium acetate. The saccharin passes

into solution as a sodium compound; the 1 : 4 compound remains undissolved.

F. von Heyden (*Br. pat.*, 1893, 10769), by crystallisation of the solution containing the mixed salts (potassium, sodium, calcium, or magnesium) of the 2 forms, by which the 1 : 4 salt remains in solution, being much more soluble than the 1 : 2 form.

Saccharin is a white crystalline powder, with a faintly aromatic odour and intense, sweet taste; 1 part in 10,000 of water can be detected by the taste. It melts at 220°. Its solubilities are: 1 part dissolves in 400 parts of cold water, 100 parts of boiling water, 25 parts of (90%) alcohol, and 120 parts of ether. It is also soluble in a mixture of ether and light petroleum. These immiscible solvents extract it from an (acidified) solution in water. It is soluble in glycerol. Water containing alkali or alkali carbonates dissolves more than pure water. As already noted, the hydrogen atom of the imino-group may be replaced by other positive radicals. Some of these derivatives are more soluble than saccharin itself and have more or less of its sweetness.

Sodium saccharin, $C_6H_4(CO)(SO_2)NNa + 2H_2O$, occurs in commerce under the name of "soluble saccharin" or "crystallose." It separates from hot water in readily soluble crystals.

COMMERCIAL SACCHARIN.

Apart from the by-products of manufacture, saccharin is liable to adulteration with diluents both organic and inorganic. Samples containing little else than inert mineral matter, such as calcium sulphate, have been found. As pure saccharin sublimes entirely at a temperature not much above its m. p., ordinary mineral adulterants are indicated by notable amounts of ash.

Sugars, glucose and starch will be left insoluble after repeatedly treating the solid sample with ether. A better separation from sugar can be obtained by repeatedly agitating the acidified aqueous solution of the sample with ether. If, after removing the ether, the aqueous layer be found, after neutralisation, to have a distinctly sweet taste, the presence of sugar is certain. The quantity can be ascertained by Fehling's solution after inverting the sugar, and preferably after removing the saccharin by ether. Saccharin does not reduce Fehling's solution.

Saccharin should not blacken when treated with cold concentrated

sulphuric acid, and even on heating the mixture to 100° for 10 minutes the colouration should merely be faint brown.

Benzoic or salicylic acid can be detected by heating a small amount of the sample with water, allowing the liquid to cool, filtering and testing the filtrate with ferric chloride. Benzoic acid will be shown by a turbidity; salicylic acid by a violet tint.

One of the usual by-products in commercial saccharin is 1–4-sulphaminobenzoic acid, $C_6H_4(COOH)SO_2NH_2$. For the detection of this, 1 grm. of the sample should be shaken with 70 c.c. of ether at 15° for a few minutes, the ether drawn off as far as possible, the undissolved portion dried and its m. p. determined. This should not be above 220°. The amino-acid is much less soluble in ether than saccharin. The amino-acid melts at about 282°.

Langbein (*Zeit. angew. Chem.*, 1896, 486) estimates the amount of *p*-sulphaminobenzoic acid in a sample of commercial saccharin by determining its heat of combustion. Saccharin has the heat of combustion 4753.1 cal. whilst that of *p*-sulphaminobenzoic acid is 4307.3 cal. The method is stated to give good results.

Reactions and Detection.—Parmeggiani (*Boll. Chim. Farm.*, 1908, **47,** 37) finds that pure saccharin has the following properties: It is not attacked by nascent hydrogen in alkaline solution, by potassium permanganate, by hydrogen peroxide, or, when cold, by the halogens. Cold nitric acid has no action, but when heated with the acid the sulphogroup is eliminated as sulphuric acid. The most sensitive precipitant for *o*-benzoicsulphinide is mercurous nitrate.

When a solution of saccharin is evaporated with potassium hydroxide and the residue is heated to 250°, salicylic acid is formed, and may be detected by rendering the solution of the residue neutral or faintly acid, and adding ferric chloride, when the characteristic violet colouration will be produced. On igniting a mixture of saccharin and potassium hydroxide or carbonate an odour of benzene is evolved, and on dissolving the residue in water acidified with hydrochloric acid, the solution gives a white precipitate of barium sulphate when barium chloride is added.

Remsen and Burton state that when *o*-benzoic-sulphinide is boiled with dilute acids, it is first converted into 1–2-*sulphaminobenzoic acid*, $COOH.C_6H_4(SO_2NH_2)$, but on continued boiling it is completely changed into *hydrogen ammonium 1–2-sulphobenzoate*, $COOH.C_6H_4(SO_3NH_4)$. By evaporating a solution of saccharin with strong

hydrochloric acid, o-sulphobenzoic acid and ammonium chloride are obtained.

The 1–4-sulphaminobenzoic acid, often present in considerable proportion in commercial saccharin, is unchanged by boiling with dilute acids.

The following are other reactions characteristic of saccharin: If 0.01 grm. to 0.02 grm. is dissolved in 10 c.c. of water containing 2 drops of a 10% sodium hydroxide solution, treated with a solution of p-diazonitroaniline, drop by drop, until the greenish-yellow colour of the liquid disappears, and then shaken with 10 c.c. of ether, the ethereal extract, when treated with 20 to 30 drops of the 10% sodium hydroxide solution, gives a fine green ring at the point of contact. On shaking, the ether turns green and the alkali yellowish-brown, whilst the addition of strong ammonia to the ethereal layer decolourises the latter, the ammonia becoming green. With a mixture of saccharin and salicylic acid the reaction gives first a red somewhat brownish ring, then a red aqueous and green ethereal layer. On addition of ammonia the ether is decolourised, whilst the aqueous liquid becomes violet, the shade of colour depending on the proportions of salicylic acid and saccharin present (Riegler, *Pharm. Centr. Halle*, 1900, **41**, 563).

Very dilute solutions of saccharin, when treated with dilute ferric chloride solution followed by hydrogen peroxide, give a violet colouration (Leys, *Compt. rend.*, 1901, **132**, 1056).

If saccharin is heated for 5 minutes at 160° to 170° with a small quantity of a mixture of 5 c.c. of phenol and 3 c.c. of sulphuric acid, and the product dissolved in water, the solution turns purple or rose-red when treated with a little sodium hydroxide solution. (Kastle, *U. S. Pub. Health and Marine Hosp. Serv. Hyg. Lab. Bull.*, 1905, **26**, 31.)

Detection of Saccharin in Foods and Beverages.—Saccharin, being an antizymotic, fulfils 2 requirements in foods and beverages— a preservative and a substitute for sugar.

A large number of methods for the detection of saccharin have been suggested, which differ almost solely in the procedure by which it is isolated. The actual identification is nearly always effected by converting it into salicylic acid which is recognised by the ferric chloride reaction. Necessarily salicylic acid, phenols, tannin, and extractive matter, which react with ferric chloride, must be removed previously. These substances are best eliminated from beverages by the method

described by Villiers and his coadjutors (*Rev. Chim. Appl.*, 1904, **7,** 144) and modified by Bianchi and di Nola (*Boll. chim. farm.*, 1908, **47,** 599). The liquid is freed from alcohol by evaporation (repeated if necessary), heated to boiling, acidified with 20 drops of 1% acetic acid per 100 c.c., and treated with excess of lead acetate solution (10 c.c. of a 20% solution per 100 c.c.). After standing for 30 minutes the excess of lead is precipitated by addition of a solution containing 10 grm. of sodium sulphate and the same weight of sodium phosphate per 100 c.c. The liquid is filtered, the filtrate concentrated to 70 or 80 c.c., acidified with 6 or 8 c.c. of 25% sulphuric acid, and extracted 3 times with pure benzene or once with a mixture of equal volumes of ether and benzene. The extract is evaporated almost to dryness and the residual liquid treated with a small quantity of ferric chloride solution (1:1,000) to test for salicylic acid. The benzene is evaporated without removing the ferric chloride, the aqueous residue acidified with 10 c.c. of 10% sulphuric acid, warmed on a water-bath and a solution of potassium permanganate added until a permanent pink colouration is produced. In this way free salicylic acid and substances which simulate or mask the colouration with ferric chloride are destroyed. When cold the liquid is extracted 3 times with pure benzene, the extract evaporated, and the residue dissolved in 2 c.c. of water. If 1 drop of this solution has a sweet taste the remainder is transferred to a test-tube, treated with 2 c.c. of sodium hydroxide solution, evaporated to dryness, and the tube immersed in a fusible-metal bath at 270° for 3 minutes. The fused residue is dissolved in 10% sulphuric acid, the solution extracted with benzene, and the benzene extract filtered and shaken with 5 c.c. of neutral ferric chloride solution (1:1,000). The formation, in the aqueous liquid, of the violet colouration characteristic of salicylic acid, indicates the presence of saccharin in the sample.

Similar methods have been proposed by Boucher and de Bounge (*Bull. Soc. Chim.*, 1903, [iii], **29,** 411), Chace (*J. Amer. Chem. Soc.*, 1904, **26,** 1627), who states that 0.005 grm. of saccharin per litre can be detected by this method, and Jorgensen (*Ann. Falsif.*, 1909, **2,** 58).

Bonamartini (*Rev. intern. Falsif.*, 1906, **19,** 39) has suggested the use of bromine water for the oxidation of tannin and precipitation of salicylic acid, but Boucher and de Bounge state that the permanganate is to be preferred.

Allen concentrates the sample, defecates with lead acetate, acidifies with phosphoric acid, and extracts with ether. The residue from the

evaporation of the ethereal solution is fused with sodium hydroxide and the product tested for sulphate. If this is found, saccharin was present. von Mahler (*Chem. Zeit.*, 1905, **29**, 32) fuses the residue with sodium instead of sodium hydroxide and tests the solution of the fused mass for alkali sulphide by means of sodium nitroprusside.

Other solvents have been suggested for the extraction. A mixture of ether and light petroleum is recommended by Delle (*Rev. intern. Falsif.*, 1900, **13**, 121), Wirthle (*Chem. Zeit.*, 1900, **24**, 1035), and Spica (*Gazzetta*, 1901, **31**, ii, 41), toluene by Tagliavini (*Boll. chim. farm.*, 1907, **46**, 645) who detects the saccharin in the extract by the formation of a white precipitate with mercurous nitrate solution, and amyl acetate by Parmeggiani (*Boll. chim. farm.*, 1908, **47**, 37).

Formenti states (*Boll. chim. farm.*, 1902, **41**, 453) that by the following method, 0.001 grm. of saccharin can be detected in 100 c.c. of milk: 100 c.c. of the sample are treated with 1 c.c. of acetic acid (sp. gr. 1.038) and the mixture heated on a water-bath for 30 minutes. The precipitated casein is filtered off and washed, the filtrate and washings acidified with 5 c.c. of sulphuric acid (sp.gr. 1.134) and extracted with 50 c.c. of a mixture of equal volumes of ether and light petroleum, a small quantity of alcohol being added towards the end of the extraction. The ether-petroleum extract is evaporated and the residue tested by any of the reactions described above. Salicylic acid, if present, will be extracted with the saccharin.

Spica (*Gazzetta*, 1901, **31**, ii, 41) detects saccharin either by converting the imino nitrogen into nitric acid and identifying this by diphenylamine hydrochloride or by hydrolysis and application of the diazoreaction.

A method of isolating saccharin from fatty oils is described by Bianchi and di Nola (*Boll. chim. farm.*, 1908, **47**, 183). For its isolation from solid foods, the latter may be extracted with dilute acid, or by gently warming with water, the aqueous or acid extract being treated as already described.

Estimation.—The proportion of saccharin present in a sample may often be found by extracting the aqueous solution several times with ether, evaporating the ether, and weighing the residue. Approximation may be often obtained by titrating the aqueous solution with decinormal sodium hydroxide, using litmus or phenolphthalein. 1 c.c. of decinormal alkali neutralises 0.0183 grm. of saccharin.

The following process was devised by Hefelmann (*Pharm. Central.*

Halle, 1895, **36,** 228); 10 grm. of the sample are heated with 100 c.c. of 73% sulphuric acid for 5 hours, the vessel being immersed in boiling water and frequently shaken. The mixture is then cautiously diluted with 100 c.c. of water, cooled, a crystal of pure 1–4-sulphamidobenzoic acid added, and the solution allowed to stand for at least 12 hours. When only small amounts of the 1–4 compound are present, it may be necessary to allow the solution to stand for several days. The 1–4 acid separates almost entirely. It is collected in a Gooch crucible provided with a double strainer and an asbestos filter, washed with water until the acid reaction is removed, dried at 100° to constant weight and weighed. The loss due to the slight solubility of the precipitate in cold water is not serious. The material should melt at from 270° to 280°.

The filtrate and washings are made up to 500 c.c. with water, 50 c.c. of this mixed with excess of magnesium oxide, and distilled. Ammonium hydroxide is formed, which is absorbed by dilute standard acid as in the Kjeldahl method. From the amount of ammonium nitrogen thus indicated the saccharin in the original material can be calculated: 1 part of nitrogen is equivalent to 13.07 parts of saccharin.

The principle of the above process is due to Remsen and Burton (*Amer. Chem. J.*, 1889, **11,** 403) who used dilute hydrochloric acid instead of the relatively strong sulphuric acid employed by Hefelmann. Reid (*Amer. Chem. J.*, 1899, **21,** 461) found that the hydrolysis is best effected by dilute hydrochloric acid, and that the ammonia can then be distilled off, after making the liquid alkaline, as in the ordinary Kjeldahl process. Reid's method is as follows: 0.5 to 1 grm. of the sample is weighed into a 100 c.c. flask and 50 c.c. of approximately normal hydrochloric acid added. The flask is fitted with an air-condenser (45 cm. long by 8 mm. diameter) and heated on a sand-bath for 2.5 hours, so that the liquid is kept gently boiling. The condenser is then removed and the liquid concentrated to about 10 c.c. and washed into a distillation-flask. 20 c.c. of a 50% solution of sodium hydroxide are added and the ammonia distilled into a known volume of standard acid, the excess being titrated with standard potassium hydroxide using cochineal as indicator. The ammonia is formed from the *o*-benzoicsulphinide (and any ammonium salts present as impurities), the *p*-sulphaminobenzoic acid not being attacked in the process. Since *o*-benzoicsulphinide is not attacked by alkali hydroxide solutions, the amount of ammonium salts present, if any, can be esti-

mated by distilling a separate portion of the sample with sodium hydroxide solution.

Proctor has employed Reid's process and gives results showing that it is quite reliable even in the presence of considerable amounts of the para-compound or of such possible impurities as toluene-o-sulphonamide (*Trans.*, 1905, **87**, 242).

Proctor finds that iodine is liberated from a solution of potassium iodide and iodate by saccharin and, more slowly, by p-sulphamino-benzoic acid, the reaction being quantitative. The powder (0.5–1.0 grm.) is weighed into a 150 to 200 c.c. flask with a well-fitting stopper, and 50 to 75 c.c. of water added. A crystal or two of potassium iodide are dropped into the mixture, 10 c.c. of a 5% potassium iodate solution added and the mixture shaken gently. Pure o-benzoic-sulphinide dissolves almost immediately, liberating an equivalent weight of iodine which is titrated against standard sodium thiosulphate solution. The presence of any large proportion of p-sulphamino-benzoic acid causes the powder to dissolve much more slowly and frequent shaking during 15 to 20 minutes may be required to effect the complete solution necessary before titration. If the proportion of the para-compound present is small, the number of c.c. of $N/10$ thiosulphate solution used, multiplied by 0.0183 gives very approximately the total weight of o-benzoicsulphinide and p-sulphamino-benzoic acid present.

A rapid, though only approximate, method of estimating the proportions of real saccharin and the para-compound in a sample, is based on the titration of 3 to 5 grm. of the latter with standard alkali, using phenolphthalein as indicator. 1 grm. of saccharin neutralises 54.6 c.c., whilst the same weight of p-sulphaminobenzoic acid requires 49.7 c.c. of $N/10$ sodium hydroxide solution. From the volume of alkali required the percentage of each substance is easily calculated (*Pharm. Post.*, 1901, **31**, 234).

Parmeggiani (*Boll. chim. farm.*, 1908, **47**, 37) states that saccharin in foods can be very accurately estimated by the following process: The liquid (or aqueous extract of a solid food) is concentrated, treated as described under *Detection* in order to remove salicylic acid and extractive matter, and extracted several times with a mixture of equal volumes of ether and light petroleum. The combined extracts are washed with water, evaporated to dryness, and the residue titrated with $N/200$ sodium hydroxide solution. For the estimation of

saccharin in foods containing benzoic acid, Testoni (*Zeit. Nahr. Genussm.* 1909, **18**, 577) recommends that the ether extract of the food should be heated at 110° to 115° to volatilise the benzoic acid. Another method is to precipitate the saccharin from an alcoholic solution of the extract, as silver saccharinate $AgC_7H_4SO_3N$ by addition of silver nitrate solution. After standing 12 hours the precipitate is collected on a Gooch crucible, washed with alcohol, dried at 100° and weighed. A method of estimating saccharin in cocoa powder, depending on the fusion of the substance, when isolated, with sodium carbonate and nitrate and determination of the sulphate formed, is described by van den Driessen Mareeuw (*Pharm. Weekblad,* 1907, **44**, 245).

CINNAMIC ACID AND ITS DERIVATIVES.

Cinnamic Acid.   β-Phenyl-acrylic Acid.

$$C_9H_8O_2 = C_8H_7CO . OH = C_6H_5 . CH:CH . COOH.$$
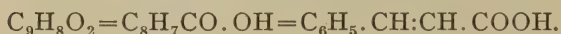
Cinnamic acid occurs free and as esters in liquid storax, Tolu and Peruvian balsams, in Sumatra benzoin, and in old oils of cinnamon and cassia, which sometimes deposit it in large crystals.

For the methods of synthesis see Miller (*Annalen,* 1877, **188**, 196) and Perkin (*Trans.,* 1877, **31**, 389). It is manufactured by the action of sodium acetate on benzylidene chloride.

Cinnamic acid crystallises in colourless, monoclinic prisms or laminæ having a sp. gr. of 1.247. It melts at 133° and distils with more or less decomposition at about 300°.

J. Kachler (*Ber.,* 1869, **2**, 512) gives the following table showing the m. p. of various mixtures of cinnamic and benzoic acids:

Cinnamic acid, %	Benzoic acid, %	M. p., °
100	0	133.3
99	1	131.8
90	10	126.6
80	20	118.0
70	30	108.2
60	40	98.7
50	50	84.3
40	60	87.1
30	70	101.4
20	80	106.4
10	90	111.5
1	99	118.2
0	100	123.3

Cinnamic acid dissolves sparingly in cold water (1 in 3,500 at 17°), but readily in boiling water, alcohol, and ether.

According to T. Bokorny, whilst cinnamic acid (in the form of 0.1% solution) is a good bactericide, the sodium salt is much less active, a 1% solution being required to show any antiseptic action. The germicidal properties of cinnamic acid are stated to be greatly enhanced if used in conjunction with a little tartaric acid.

Reactions.—Cinnamic acid, when slowly heated alone, or more readily if heated with lime, splits into carbon dioxide and cinnamene, C_8H_8, a small quantity of stilbene, $C_{14}H_{12}$, being also produced.

A neutral solution of a cinnamate gives a precipitate with manganous salts, at first white but afterwards becoming yellow and crystalline (benzoates give no precipitate). The precipitate formed with ferric salts is yellow.

Cinnamic acid is also distinguished from benzoic acid by the smell of bitter-almond oil developed on warming it with chromic acid mixture. The same odour is produced by boiling cinnamic acid with water and lead dioxide, the latter substance gradually becoming yellow, and being partially converted into lead benzoate.

When fused at a moderate temperature with potassium hydroxide cinnamic acid is split up with evolution of hydrogen and formation of potassium acetate and benzoate—$C_9H_8O_2 + 2KHO = KC_2H_3O_2 + KC_7H_5O_2 + H_2$. The presence of an acetate in the product is a proof of the existence of cinnamic acid in the original substance.

Benzoic acid may be separated from cinnamic acid by crystallisation from boiling alcohol. The acids may also be separated by distillation in a current of steam, when benzoic acid nearly free from cinnamic acid passes over. By careful sublimation, the benzoic acid may also be completely separated, as little cinnamic acid volatilises below 200°.

Cinnamic acid may be detected in presence of benzoic acid by Jorissen's reaction (compare p. 407).

For the detection of benzoic acid in cinnamic acid Lunge (*Chemisch-technische Untersuchungsmethoden*, 1905, **3**, 860) gives the following method: 1 grm. of the sample is shaken for an hour with 100 c.c. of water at 20° and the liquid filtered. 50 c.c. of the filtrate are titrated with $N/10$ sodium hydroxide solution using phenolphthalein as indicator. If the sample is pure, the volume of alkali used will be 1.4 c.c., whilst in the presence of benzoic acid, which is more than

5 times as soluble as cinnamic acid, a larger volume will be required. Pure benzoic acid by this process gives a filtrate 50 c.c. of which neutralise 11.2 c.c. of $N/10$ alkali. By this test 1% of benzoic acid can be detected.

Estimation.—Lunge (*loc. cit.*) estimates the cinnamic acid in a sample by dissolving 1 grm. in 10 c.c. of N-alkali and titrating back with N-acid. 1 c.c. of N-sodium hydroxide solution corresponds to 0.148064 grm. of cinnamic acid.

Cinnamic acid combines with 2 atoms of bromine when treated with excess of this reagent under suitable conditions. In this way cinnamic acid may be estimated in admixture with benzoic acid, which does not take up bromine directly. The following directions are given by De Jong (*Rec. trav. chim.*,1909, **28**, 342). About 2 grm. of mixed acids are dissolved in carbon disulphide, the solution treated with bromine and allowed to stand for 24 hours. The solvent and excess of bromine are then distilled off and the residue dissolved in ether. The ethereal solution is evaporated to dryness at ordinary temperature and the residue dried over sulphuric acid *in vacuo*. The solid is then powdered and heated at 100° in Ruber's apparatus (*Anal. u. Konst. org. Verb. von. H. Meyer*, 1903, p. 14) and the residual phenyldibromopropionic acid weighed. It is claimed that the separation is quantitative. The estimation may also be made as described under Salicylic Acid (p. 480). Bigelow recommends the following process for detecting cinnamic acid in foods (*U. S. Dept. Agric. Bull. No.* 122, 1909, 77). A mixture of 100 grm. of the food with 100 c.c. of water and 5 c.c. of sulphuric acid (1:5) is extracted three times with (50 c.c., 25 c.c., and 25 c.c.) chloroform, and the combined extracts evaporated to dryness after being rendered alkaline with ammonia. The residue is heated to boiling with 5 c.c. of dilute chromic acid mixture (1 part of dilute sulphuric acid saturated with potassium dichromate, and 7 parts of water). The odour of benzaldehyde is most apparent after cooling the liquid so that sulphuric acid fumes are no longer evolved. The method will detect 0.025 grm. of cinnamic acid per kilogram.

CINNAMIC ESTERS.

Methyl cinnamate, $CH_3.C_9H_7O_2$, forms crystals melting at 33° and boiling at 263°. It is an important constituent of the essential oil of the rhizomes of *Alpinia Malaccensis*, and is also present in the leaves

of the same plant.   Other oils derived from plants of the same species probably contain this ester.

Ethyl cinnamate, $C_2H_5.C_9H_7O_2$, is produced by distilling together cinnamic acid, alcohol, and strong sulphuric acid; or by saturating a strong solution of cinnamic acid in alcohol with hydrogen chloride.   It is a limpid liquid having sp. gr. 1.3 and b. p. 271°.

Benzyl Cinnamate.   Cinnamein. $C_7H_7.C_9H_7O_2$.   This substance exists ready-formed in Peru and Tolu balsams.   It may be obtained with some admixture of cinnyl cinnamate by treating the former substance with carbon disulphide, separating the insoluble matter, and distilling off the solvent from the solution.

Benzyl cinnamate has an agreeable taste and feeble aromatic odour, resembling that of Peruvian balsam, but without the empyreumatic smell observable in the latter.   It is commonly described as an oily liquid which is liable to solidify with conversion into a crystalline isomeric substance called metacinnamein.   But when obtained pure by boiling together benzyl chloride, alcohol, and dry sodium cinnamate, it forms short shining white prisms, m. p. 39°, which may remain liquid for a considerable time if cooled to 0°. Benzyl cinnamate has sp. gr. 1.098 in the liquid state, and b. p. 225° to 235° with slight decomposition.   It is nearly insoluble in water, but is readily dissolved by alcohol, ether, carbon disulphide, etc.

By long exposure to air and light, benzyl cinnamate acquires an acid reaction.   It is readily saponified by alcoholic potassium hydroxide with formation of potassium cinnamate and benzyl alcohol, $C_7H_7.OH$.

Phenyl cinnamate, $C_6H_5C_9H_7O_2$ has m. p. 72.5° and b. p. 206° 15 mm.; at ordinary pressure it boils with decomposition.   *Phenyl propyl cinnamate* occurs in small amount in Sumatra benzoin, in storax, and yellow resin.

Cinnamyl Cinnamate.   Styracin. $C_9H_9.C_9H_7O_2$.   This substance occurs together with benzyl cinnamate in liquid storax, and Peru and Tolu balsams.   It crystallises in tufts of beautiful prisms, m. p. 44°, which are devoid of smell or taste.   It distils without decomposition in steam heated to 180°.   Cinnamyl cinnamate is insoluble in water and but sparingly soluble in cold alcohol or light petroleum, but is easily soluble in ether or carbon disulphide.   When treated with alcoholic potassium hydroxide it is saponified with formation of potassium cinnamate and

Cinnamyl Alcohol, Styryl Alcohol, Styrone, β-Phenylallyl-

alcohol, $CHPh : CH.CH_2.OH.$ When cinnamyl cinnamate is cautiously distilled with aqueous potassium hydroxide, a milky distillate is obtained, and on saturating it with common salt the cinnamyl alcohol forms a creamy or oily layer on the surface. It may also be extracted from the distillate or the original liquid by agitation with ether.

Cinnamyl alcohol forms soft, silky needles, m. p. 33°, b. p. 250°, having a sweet taste and an odour of hyacinths. It is soluble in about 12 parts of cold water, a hot saturated solution becoming milky on cooling and remaining so for several hours, when the cinnamyl alcohol separates in crystalline needles, very soluble in alcohol and ether.

Cinnamyl alcohol possesses valuable antiseptic properties, being as powerful in this respect as thymol.

Cinnamyl alcohol is converted by cautious oxidation into cinnamic aldehyde and cinnamic acid. With chromic acid mixture it becomes hot and yields cinnamic acid, which separates on the surface, and on heating this becomes further oxidised to benzaldehyde.

Cinnamene, styrene, or phenyl-ethylene $(C_6H_5)CH:CH_2$, exists in small quantity ready-formed in liquid storax (page 462), and may be extracted by distilling the balsam with water to which sodium carbonate has been added to neutralise the free cinnamic acid. The hydrocarbon passes over with steam, and collects as an oil on the surface of the distillate. Cinnamene may also be obtained synthetically, and, as stated above, by heating cinnamic acid alone or in admixture with lime or baryta. The reaction in the latter case is exactly parallel to that by which benzene is produced from benzoic acid and methane from acetic acid.

Cinnamene is a colourless, mobile liquid, of sp. gr. 0.925 at 0°, having a pleasant aromatic odour. It remains fluid at —10° and boils at 144°, the temperature of the contents of the retort being liable to rise suddenly from formation of metacinnamene.

Stilbene, or diphenyl-ethylene, $(C_6H_5)CH.CH(C_6H_5)$, crystallises in nacreous plates, m. p. 124°, b. p. about 306°. It unites with bromine to form a dibromide, $C_{14}H_{12}Br_2$, of which 2 stereoisomeric modifications exist, the α, m. p. 237°, and the β, m. p. 110 to 110.5°

CINNAMIC ALDEHYDE. $CHPh : CH.CHO.$

This occurs in oils of cassia and cinnamon, of which it constitutes the greater part.

Hanuš (*Zeit. Nahr. Genussm.*, 1904, **7,** 669) found the following amounts of cinnamaldehyde in the different varieties of cinnamon: Ceylon cinnamon, 1.74 to 2.19%; cassia cinnamon, 2.08 to 3.81%; buds of the latter, 3.70 to 6.00%; cinnamon chips 1.23 to 1.42%.

For the synthesis of cinnamaldehyde see Peine (*Ber.*, 1884, **17,** 2117).

Cinnamaldehyde is a colourless oil, rather denser than water. It may be distilled in a vacuum, or with water free from air. On exposure to the air, it quickly becomes yellow and resinous, and acquires an acid reaction. It rapidly absorbs oxygen, especially in presence of moisture, and is converted into cinnamic acid. Chromic acid converts it into benzoic and acetic acids.

Estimation.—Schimmel & Co. estimate cinnamaldehyde in cinnamon and cassia oils by the following process:

A special flask with a somewhat flat-bottomed bulb and long neck is used. The bulb holds about 100 c.c. The neck is about 13 cm. long, has a calibre of 8 mm., and is graduated to read to 0.1 c.c. The total capacity of the neck is a little over 6 c.c. The zero-mark is slightly above the point at which the neck joins the bulb. 10 c.c. of oil are transferred to the flask and 10 c.c. of a 30% solution of sodium hydrogen sulphite added. The mixture is shaken and immersed in boiling water. When the mass has melted, more sodium hydrogen sulphite solution is added and, still shaking, the addition of small amounts of sulphite is continued until the volume of the mixture is about 75 c.c. The heating is continued until no more solid particles are present and the odour of cinnamaldehyde has disappeared. When the clear oil floats upon the salt solution, the flask is removed from the bath, and when the contents are cold, sufficient sulphite solution is added to raise the lower limit of the oily layer to zero. The amount of oil is then read off, and by deducting this number from 10, the volume of cinnamaldehyde in the sample is obtained. As the sp. gr. of the aldehyde and other constituents are nearly the same, the reading may be taken as percentage by weight.

Burgess (*Analyst*, 1904, **29,** 78) advocates a similar method, but uses neutral sodium sulphite and neutralises the alkali as it is formed in the action by the gradual addition of acetic acid, phenolphthalein being present as indicator. The action is complete when the liquid ceases to become alkaline on standing after further addition of sulphite.

The process employed by Pouchand (*Schweiz. Woch. Chem. Pharm.*, 1904, **42,** 146) is based on the same principle.

Sadtler, whose method is adopted in the United States Pharmacopœia, follows Burgess's directions, but estimates the aldehyde by determination of the amount of alkali formed in the reaction. 12 drops of the oil are weighed into a 150 to 200 c.c. flask, mixed with 5 c.c. of water and a few drops of rosolic acid solution, and the liquid exactly neutralised with $N/10$ alkali. 50 c.c. of a 20% sodium sulphite solution are added and the flask immersed in boiling water. Sufficient $N/2$ hydrochloric acid is gradually added to keep the liquid neutral, whilst the flask is continuously heated and shaken. When a condition of permanent neutrality is reached, the volume of $N/2$ acid used, is noted. A blank experiment is made using exactly the same quantities of reagents, but no aldehyde. The volume of $N/2$ hydrochloric acid required is deducted from that used in the estimation. Each c.c. of difference corresponds to 0.033 grm. of cinnamaldehyde.

J. Hanuš (*Zeit. Nahr. u. Genussm.*, 1903, **6**, 817) found that cinnamaldehyde, both pure and as it occurs in cinnamon and cassia oils, may be quantitatively precipitated in the form of semioxamazone,

$$C_6H_5.CH:CH.CH:N.NH.CO.CO.NH_2,$$

by treating an aqueous suspension with a solution of semioxamazide in hot water. 0.10 grm. of the aldehyde is weighed off, emulsified by agitation with 100 c.c. of water treated with 0.25 to 0.35 grm. of semioxamazide in 15 c.c. of hot water; the mixture is well shaken together, occasionally for 3 hours, then allowed to stand for 24 hours. The crystalline cinnamaldehyde semioxamazone is then collected on a tared Gooch filter, washed with cold water, dried at 105° for about 4 or 5 hours, then weighed. The weight of semioxamazone multiplied by the factor 0.6083 gives the amount of cinnamaldehyde present. For the estimation of the amount of aldehyde in cinnamon and cassia oils from 0.15 to 0.2 grm. should be employed.

To estimate the amount of cinnamaldehyde in cinnamon or cassia barks, from 5 to 8 grm. of the finely ground material are distilled with steam until about 400 c.c. of distillate have been collected. The volatile oil is extracted from the distillate by shaking out 3 or 4 times with ether, and after distilling off the ether, the oil is emulsified and treated with semioxamazide as described above. By this method commercial cinnamaldehyde has been found to yield from 99.21 to 100.66% commercial cinnamon oil from 46.78 to 80.51% of cinnamaldehyde; Ceylon cinnamon oil from another source, 79.05 to 80.33%. Syn-

thetic cassia oil, 95.19 to 95.58% of cinnamaldehyde. Cinnamon bark was found to yield from 1.75 to 2.04% of aldehyde.

It is claimed that the method gives results more accurate than those of the sulphite absorption process generally employed. With commercial cinnamaldehyde, Allen obtained figures which were nearly 5% lower than those given by the sulphite method. With the natural oils, however, the latter method gave results from 4 to 6% lower than this gravimetric process.

Oil of Cinnamon. Oil of Cassia.—The volatile oil of cinnamon is prepared by distilling the chips and refuse bark with water.

The oil of Ceylon cinnamon is a pale yellow or reddish liquid, becoming red-brown and thicker on exposure to air, and finally separating crystals of cinnamic acid. It has a strong, but agreeable, cinnamon odour, and a sweet, pungent, aromatic taste. The sp. gr. increases with the age of the oil. It remains clear at —10°, but at a lower temperature (—20°) separates a stearoptene. It is readily soluble in alcohol, but not in cold light petroleum, and when fresh is neutral to litmus, becoming acid by oxidation.

In addition to cinnamaldehyde, cinnamon oil contains small amounts of eugenol, phellandrene, methyl *n*-amyl ketone, pinene, cymene, furfural, benzaldehyde, nonylaldehyde, cuminaldehyde, caryophyllene, linalool, linalool *iso*butyrate, and hydrocinnamaldehyde (Walbaum and Hüthig, *J.pr. Chem.*, 1902, [ii], **66,** 47). Schimmel & Co. prepare an artificial cinnamon oil by mixing cinnamaldehyde with small quantities of these substances.

Some cinnamic acid may be present, the amount depending on the age of the sample, as the acid is produced by the oxidation of the aldehyde. The so-called "cassia stearoptene," described by Rochleder, is found only in old cassia oil. It is a complex aldehydic derivative. Cinnamyl acetate is sometimes present.

Hirschsohn (quoted from *Phar. Zeit. f. Russl.*, 1891, **30,** 790; by Gildemeister and Hoffmann, *"Volatile Oils,"* p. 386) found that owing to the solvent action of cinnamic acid on lead, the oils are apt to become contaminated with that element from the leaden vessels in which they are often imported. As the oils are used for food-flavours and sometimes in medicines for internal use the presence of lead is a danger.

According to the British Pharmacopœia, oil of cinnamon should have sp. gr. 1.025–1.040, should dissolve in 2 volumes of 70% alcohol,

and should contain at least 50% of aldehyde. The United States Pharmacopœia requires not less than 75% cinnamaldehyde, whilst the German Pharmacopœia puts the limit at 70%.

Adulterations of Oil of Cinnamon.—Oil of Ceylon cinnamon is liable to be adulterated with oil of cassia and oil of cinnamon leaves. The important data for detecting these are the amounts of eugenol and cinnamaldehyde. Parry found many samples of cinnamon oil in the London market which had been adulterated with a mixture of cinnamon-leaf oil and synthetic cinnamaldehyde added in large proportion to the genuine oil. He gives the following figures yielded by adulterated oils of this type:

Sp. gr.	% Cinn. ald.	% Eugenol
1.036	25.5	45
1.042	24.8	47
1.051	27.0	49

A qualitative test for eugenol is often of use. A drop of genuine cinnamon oil dissolved in 5 drops of strong alcohol produces a pale green with ferric chloride, but leaf oil produces a deep blue.

When the amount of cinnamaldehyde is low an estimation of the eugenol should be made. The most accurate method is that described by Thoms (*Ber. Pharm. Ges.*, 1891, **1**, 279). The oil is mixed in a beaker with 4 volumes of 15% sodium hydroxide solution and treated with excess of benzoyl chloride. Esterification takes place rapidly if the mixture is well stirred. After cooling, water is added and the crystals melted, washed with warm water, and dissolved in a small quantity of hot 90% alcohol. The solution is shaken whilst being cooled to 17°, so that the benzoyleugenol separates in small crystals. The latter are collected on a tared filter, washed with a small known volume of alcohol, dried at 101°, and weighed. A correction must be made for the amount of benzoyleugenol dissolved in the (90%) alcohol, 100 c.c. of which at 17° dissolve 2.20 grm.

Umney (*Pharm.J.*, 1895, [iii], **25**, 949) has suggested a simpler process, namely, to determine the diminution of volume resulting upon shaking the sample with a 5% solution of potassium hydroxide. The alkali dissolves some of the other constituents, but approximations can be made by the method. Adulteration may be assumed if the "eugenol content" is over 10%.

Pool (*Pharm. Weekblad*, 1903, **40**, 1101) states that the presence of 5% of oil of cloves can be detected in oil of cinnamon by means of Jacquemin's test. 1 c.c. of a dilute solution of aniline is treated with sodium hypochlorite solution until the liquid assumes a violet colour, when a drop of the oil is added. If the cinnamon oil is pure a dirty violet solution is obtained on shaking, which after diluting with water gives a clear violet filtrate, whilst in the presence of oil of cloves a green filtrate is obtained.

The oil of Chinese cinnamon, commonly known as *oil of cassia,* closely resembles the Ceylon product, except that its colour is deeper, its odour less delicate, its taste less sweet, and its sp. gr. somewhat higher—usually between 1.055 and 1.065. It is only slightly optically active, sometimes inactive. It should contain 70% cinnamaldehyde, and even then may not be of high quality, as good samples contain 75% or even 80%. In the London market the oil is graded by its aldehyde content, being sold as 70 to 75%; 75 to 80%; 80 to 85%.

A good cassia oil will contain not less than 75% of cinnamaldehyde. Only in rare instances does it rise above 90%. Gildemeister and Hoffmann ("*Volatile Oils,*" p. 389) state that genuine oils from China have been noted in which the aldehyde content was below 50%, yet no adulteration could be recognised. The explanation of this could not be positively ascertained.

Oil of cassia is soluble in 3 to 4 volumes of 70% alcohol, and in all proportions of 90% alcohol. It gives a brown colouration with ferric chloride and forms a crystalline mass when shaken with an equal volume of nitric acid.

Adulterations of Oil of Cassia.—Adulterations of cassia oil, practised in former years with fatty oils, cedar-wood oil, and gurjun balsam, were easily detected, as the sp. gr. was lowered by the adulterants and the free solubility in 80% alcohol was prevented. Cedar-wood oil and gurjun balsam have a strong lævo-rotation.

Adulteration with a mixture of colophony and petroleum cannot be detected by these data. Schimmel & Co. (*Semi-annual Rep.*, Oct., 1889, 15; also "*The Volatile Oils,*" Gildemeister and Hoffmann, p. 387) devised the following test for detecting this admixture:

50 grm. of cassia oil are weighed in a tared fractionation flask. A tube 1 metre long is attached as a condenser, and the oil is distilled with direct flame. At first, water passes off with crepitation, then the temperature rises rapidly to 240° and the bulk of the oil distils between

240° and 280°.   When white fumes appear, indicating the beginning of decomposition of the residue, the distillation is stopped.   The temperature may rise to 280° to 290° at this time.   The flask is cooled and weighed.   A good oil leaves a residue viscid and tough and not more than 10% of the original oil.   The adulterated oil leaves a hard, brittle residue weighing more than 10%.   The oil forms a clear solution with 70 to 80% alcohol.   If petroleum is present, the mixture with such alcohol is turbid, and on standing some of the petroleum products separate.

Cassia oil that contains colophony and petroleum is soluble in 80% alcohol, but if only the latter is present the solution is turbid, the petroleum separating in oily drops.   The following additional tests are taken from the work noted above:

Gilbert (*Chem. Zeit.*, 1889, **13**, 1406) suggests heating several grm. of the sample in a watch-glass in a drying oven at 110° to 120° to constant weight.   He also states that the acid number is of value.   An oil which upon distillation left 6% of residue had an acid number of 13. On adding 20% of colophony (having an acid number of 150) the acid number of the mixture was 40.   An oil yielding 28% of residue had an acid number of 47.

Hirschsohn (*Pharm. Zeit. f. Russl.*, 1890, **29**, 255) uses lead acetate as follows:

1 c.c. of the sample is added to 3 c.c. of 70% alcohol, and this is mixed, drop by drop, with a freshly prepared solution of lead acetate in 70% alcohol until the volume of the latter solution is half that of the oil solution.   A precipitate shows colophony.   Hirschsohn states that as little as 5% can be thus detected.

Oil of Cinnamon Leaves.—This is obtained by distilling the leaves of Ceylon cinnamon, but was at one time sold as oil of cinnamon root. Schimmel & Co. first pointed out the source.   A product formerly sold as cinnamon-leaf oil has disappeared from commerce, and the true oil under its proper name has taken its place.

Oil of cinnamon leaves is a mobile, nearly colourless liquid, with an odour recalling both cloves and cinnamon.   The sp. gr. ranges from 1.044 to 1.065.   The oil has slight optical activity—sometimes negative, sometimes positive.   The chemical composition is not clearly made out, but it contains eugenol and only a small amount of cinnamaldehyde.

COUMARIN,

$$C_6H_{11} \begin{cases} [1]\ CH:CH \\ \qquad\quad | \\ [2]\quad O.CO \end{cases}$$
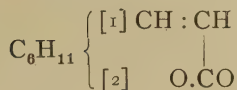
This is sometimes called "tonka-bean camphor." It is the odor-iferous ingredient of tonka, the seed of several species of *Dipteryx*, and also occurs abundantly in the leaves of *Liatris odoratissima*. It occurs also in the leaves of several other plants. Coumarin forms colourless crystals, m. p. 67°, having an odour recalling that of vanillin but not so pleasant. It is very sparingly soluble in cold water, more so in cold alcohol (13 parts to 100 of alcohol at 16°); in hot alcohol it is freely soluble. It can be prepared synthetically by the interaction of sodium acetate, salicylic aldehyde, and acetic anhydride (Perkin, *Annalen*, 1868, **147,** 230).

Kastle (see page 431) found that when the phenolsulphonic test for saccharin is applied to vanillin, the mixture becomes yellow and when the mass is heated to 160° for some minutes it becomes red and finally black. The solution of the mass in water becomes red on addition of sodium hydroxide. Coumarin gives no colour.

Coumarin is used in the preparation of perfumes, being mixed with other odoriferous principles, but its most important application from a practical analytic point of view is as an adulterant and substitute for vanillin (see under "Vanillin").

Coumaric Acids.—Hydroxycinnamic acids, $OH.C_6H_4.CH:CH.CO_2H$. 3 isomeric forms are, of course, known, respectively, 1–2, 1–3, and 1–4. The 1–2 form occurs in the leaves of species of *Meli-lotus* and in *Angræcum fragrans*. It can also be prepared by boiling coumarin with strong solution of potassium hydroxide or sodium ethox-ide. It crystallises in colourless prisms, m. p. 208° (decomp.), which are freely soluble in water and alcohol. Solutions of alkali coumarates show a bright green fluorescence. By fusion with potassium hydroxide, 1–2 coumaric acid is converted into salicylic and acetic acids. By the action of nascent hydrogen it is converted into melilotic acid.

1–4 coumaric acid occurs in small proportion in red acaroid resin, partly free and partly as a complex ester, and in larger proportion in yellow acaroid resin. Esters of this acid are also found in Cape aloes and in the resin of *Picea vulgaris*. The acid can be obtained by hydrolysis of a glucoside *naringin*, which occurs in the blossoms of

Citrus decumana, and may also be obtained by careful oxidation of 1–4 hydroxy-benzaldehyde.

Melilotic Acid.—1–2 hydrocoumaric acid, $OH.C_6H_4CH_2.CH_2$-(COOH), is obtained by the action of sodium amalgam on 1–2 coumaric acid or on coumarin. It occurs in association with coumarin in yellow melilot (*Melilotus officinalis*). It melts at 82° to 83° and produces a bluish tint with ferric chloride. It yields salicylic and acetic acids when fused with potassium hydroxide. When distilled alone, it is converted into its lactone or anhydride, *hydrocoumarin,*

$$C_4H_6 \begin{cases} CH_2\text{-}CH_2 \\ O\text{---}CO \end{cases}, \text{ m. p. } 25°, \text{ b. p. } 272°.$$ It can be regenerated by boiling with water.

Ferulic acid, $C_{10}H_{10}O_4$, m-*methoxy*-p-*hydroxycinnamic acid,* CH:CH.CO$_2$H
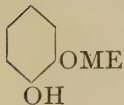
occurs in the resins of *Pinus Laricis* asafœtida, and OME OH

opoponax. It can be isolated from asafœtida by mixing the alcoholic solution with an alcoholic solution of lead acetate. Lead ferulate is precipitated, which is decomposed by means of dilute sulphuric acid not in excess, the watery liquid is decolourised with animal charcoal and the acid and the crystalline residue taken up with hot alcohol and allowed to crystallise out.

Ferulic acid reduces Fehling solution, and gives a dark yellowish-brown precipitate with ferric chloride.

Ferulic acid is related to *umbellic* acid, the lactone or anhydride of which, "*umbelliferone,*" "*hydroxycoumarin,*" occurs in asafœtida and galbanum resins and in the bark of the *Daphne mezereum.*

AROMATIC BALSAMS.

The aromatic "balsams" are such of the oleo-resinous exudations of plants as contain benzoic or cinnamic acid, and yield cinnamic or benzoic methyl or ethyl esters by dry distillation. The term "balsam" is misapplied to "Canada balsam" and "copaiba balsam," which are true turpentines and do not contain or yield benzoic or cinnamic acid.

The aromatic balsams of practical interest are gum benzoin, Peruvian balsam, Tolu balsam, and liquid storax. The first of these will be conveniently considered separately, and the others conjointly under the head of "Cinnamic Balsams."

Gum Benzoin.—Gum Benjamin. The greater part of the benzoin of commerce comes from the *Styrax benzoin*, a tree of the East Indies. Several varieties of the balsam are known of which the more important are: Siam and Sumatra benzoin (from the *S. benzoin*); Penang benzoin (probably from the *S. subdenticulata*); Palembang benzoin (source uncertain, but not from *S. benzoin*); Padang benzoin (source uncertain).

Siam benzoin is the finest variety and occurs in tears, or masses consisting of loosely agglutinated tears, yellow, reddish, or brown externally, and translucent, milk-white, or almond-like internally. It sometimes occurs in brownish lumps, which when broken present an amygdaloid appearance from the white tears imbedded in the darker resinous matter. Siam benzoin melts at 75°. This variety is never enveloped in cotton cloth.

Siam benzoin is mostly composed of a mixture of benzoresinol benzoate and siaresinotannol benzoate, the latter being the more abundant. Among other ingredients are cinnamyl benzoate, or benzyl benzoate (0.3%), vanillin (0.15%), free benzoic acid, which may be as high as 15%, and a small amount of impurities (Lüdy, *Arch. Pharm.*, 1893, **231**, 461. See also Reinitzer, *Zeit. angew. Chem.*, 1909, **22**, 1904.) As a rule, cinnamic acid or cinnamic esters do not occur in Siam benzoin, which fact serves to distinguish it from the Sumatra and Penang sorts; but some observers report samples of Siam benzoin in which cinnamic acid or its esters exist.

It should leave practically no ash.

Sumatra benzoin has a weaker and less agreeable odour than that of Siam benzoin. It occurs in large rectangular blocks, marked with the impression of a mat and covered with a white linen cloth. When broken, few but large white tears are seen in it. It is generally composed of brown resiniform matter with numerous small white chips or pieces intermixed, which give it a granitoid appearance. The white portions melt at 85° and the darker portions at 95°.

Sumatra benzoin consists principally of a mixture of a small amount of benzoresinol cinnamate and much benzoresinotannol cinnamate. The remaining ingredients are free benzoic acid, styrol, traces of benzaldehyde, benzene, vanillin 1%, phenylpropyl cinnamate (about 1%), cinnamyl cinnamate (styracin) (2–3%) (Lüdy, *Arch. Pharm.*, 1893, **231**, 43).

The part soluble in ether when ignited leaves 0.01% ash.

Cinnamic acid, indicated by the production of an odour of benz-aldehyde on heating the benzoin with chromic acid mixture, is said by Muter to be characteristic of the Sumatra product. He gives as specially distinctive characters of Siam benzoin: the production of a cherry-red benzoin when sulphuric acid is added to the residue left on evaporating the solution of the benzoin in light petroleum; the com-plete solubility of the sample in chloroform, but not in ether; and the lower m. p.

Palambang benzoin appears to be in the main similar to Siam benzoin in composition.

Padang Benzoin.—The composition of this is not well made out, but it seems to contain no cinnamic acid or ester thereof.

Penang benzoin closely resembles the Sumatra variety, but occa-sionally differs from it in colour, and more so in odour, which then sug-gests that of storax.

It contains cinnamic esters.

Qualitative Tests.—Gum benzoin always contains more or less bark and similar matters, and in inferior specimens these are present in very large proportion. With the exception of these impurities, benzoin should dissolve in 5 times its weight of alcohol. The resultant tincture from Siam benzoin has a distinct red colour, whilst that yielded by the other varieties is brown or yellowish-brown. On addition of water, the liquid becomes milky, and the odour peculiar to the particular variety is readily perceived. That of Siam benzoin is pleasantly balsamic and similar to vanilla; Penang benzoin often smells like storax; whilst the odour of Sumatra benzoin is fainter, less pleasant, and distinct from either of the former.

The presence of cinnamic acid may be recognised by the odour of benzaldehyde (bitter-almond oil), developed on adding potassium permanganate to the hot liquid obtained by boiling the benzoin with milk of lime and filtering. Or the tincture of benzoin may be treated with water, and the liquid, filtered from the precipitated resin, treated with a solution of permanganate or bleaching powder. Another method is to triturate the benzoin with lead dioxide and distil the mixture with water.

The United States Pharmacopœia (1900–1905, 8th Decennial Rev.) makes no specific distinction of the varieties of benzoin, but mentions Siam, and Sumatra benzoin. The official article is required to dis-solve almost wholly in 5 times its weight of warm alcohol (95% by

volume), the solution being acid to litmus. It must be entirely soluble in a solution of potassium hydroxide or sodium hydroxide and must not contain more than 2% of ash.

Analysis.—K. Dieterich (*Anal. d. Harze*, etc.) has devised a process applicable to benzoins in the commercial condition. This includes the estimation of ash and of data termed, respectively, "indirect acid number," "cold-saponification number," and "ester number." The last value is derived from the first two. The procedures are as follows: The weighed portions should be taken from a comparatively large amount of the material that has been finely powdered and well mixed.

Indirect Acid Number.—1 grm. is mixed in a flask with 10 c.c. of half-normal alcoholic alkali and 50 c.c. of 96% alcohol. The mixture is allowed to stand exactly 5 minutes, and then titrated with half-normal sulphuric acid and phenolphthalein until the solution is yellow, and a fresh portion of the indicator does not turn red on being dropped into the liquid, and the sodium sulphate separates readily. The supernatant liquid must be yellow. The c.c. of alkali neutralised by the sample, multiplied by the 28.08, gives the *acid number*.

Cold-saponification Number.—1 grm. of the sample is placed in a glass-stoppered flask with 20 c.c. of half-normal alcoholic alkali and 50 c.c. of light petroleum (sp. gr. 0.700). The flask, tightly closed, is allowed to stand for 24 hours at room temperature; after dilution with alcohol, the liquid is titrated with half-normal sulphuric acid and phenolphthalein. The c.c. of alkali neutralized, multiplied by 28.08, gives the cold-saponification number.

The ester number is the difference between the above data.

Dieterich gives the following as the limits of values with pure samples of the different benzoins:

	Siam	Sumatra	Palambang	Padang	Penang
Ash	0.03–1.5%	0.0–1.5%	1.1–4.02%	1.07%	0.38–0.77%
Ind. A-N	140–170	100–130	113.4–130.9	121.8–124.6	121.8–137.2
Cold-S-N	220–240	180–230	198–219.8	201.6–205.8	210–296.8
E-N	50–75	65–125	84–91	79.8–81.2	87.5–91.7
Sol. in 96% alcohol	95%	70–80%	91%	....	94%

Dieterich found that the above data are more or less influenced by several of the usual adulterations of benzoin. Dammar and storax depress the acid number; turpentine depresses the cold-saponification and ester numbers; colophony depresses the acid number, but the effect

is noticeable only when comparatively large amounts are present. For special tests for colophony, see under that substance.

The *Helfenberger Annalen* for 1903 (quoted by *Chem. and Drug.*, 1904) gives the following data from a sample of Siam benzoin, but the details of the methods used are not available:

Acid value.................................... 126.2
Ester value.................................... 96.4– 95.0
Saponification value........................... 221.2–222.6
Ash... 0.27%
Insoluble in spirit............................ 3.6%

The estimation of the cinnamic acid may be approximately effected as indicated on page 438. As much as 11% has been found.

Gum benzoin often contains from 12 to 14% of benzoic acid, but occasionally 18 or 20% is reached. The proportion present may be ascertained by the following sublimation process: The sample is powdered, mixed with sand, and the mixture heated in a beaker or earthenware jar, furnished with a cap of thin filter-paper pierced with small holes. Over this is placed a cone or hood of stout paper. The benzoic acid sublimes and condenses on the inside of the hood, any oil and impurities being retained by the diaphragm of filter-paper.

Another method for the approximate assay of gum benzoin is to digest 10 parts of the powdered gum with 6 parts of slaked lime and 100 parts of water. After 6 hours, the liquid is boiled, filtered, and the residue washed. The filtrate is concentrated, rendered strongly acid with hydrochloric acid, and thoroughly cooled. The precipitated benzoic acid is filtered off, washed with a little water, and dried between folds of blotting-paper. The small quantity of acid retained in the mother liquor may be extracted by agitation with chloroform, and the residue left by the spontaneous evaporation of the chloroform may be added to the main quantity of benzoic acid. A preferable plan is to agitate the acidified liquid at once with chloroform, without filtering off the precipitated benzoic acid, and subsequently to recover the benzoic acid from its chloroform solution by the spontaneous evaporation, of the solvent, assisted by a current of dry air from a bellows. If ether be substituted for the chloroform, the product will contain a small quantity of water and the estimation will be too high. In any case, the benzoic acid extracted by chloroform or ether from Siam benzoin will be liable to contain vanillin.

Tincture of Benzoin.—This is a simple solution of benzoin in alcohol of about 95%; usually the proportion is 1 of benzoin to 5 of

alcohol.   Compound tinctures are also used.   The assay of these prep-
arations is not much understood.   For the compound tincture pre-
pared according to the British Pharmacopœia it has been claimed that
it will be of such strength that 10 c.c. will leave not less than 1.8 grm.
of residue on evaporation.   Owing to the volatility of some of the in-
gredients, it is difficult to evaporate to constant weight.   E. Dowzard
(*Chem. and Drug.* 1904, **64,** 327) states that the following process will
give good results:

2 c.c. of the sample are placed in a tared flat-bottomed nickel basin
(diameter about 6 cm.); to this 0.1 grm. of recently ignited mag-
nesium oxide in fine powder is added; the mixture is worked into a
smooth condition with a small glass rod, which should be weighed with
the basin.   After allowing the mixture to stand for about 15 minutes,
the alcohol is slowly driven off, stirring continually.   The basin is
then placed in a water-oven, and its contents dried at 99° to 100° for 4
or 5 hours.   For drying purposes Dowzard uses an oven through
which a slow current of dry air passes, a high vacuum being at the same
time maintained.   If an ordinary drying-oven is used, a longer time will
be required than when using a vacuum apparatus.   Before taking out
of the oven, a cap of filter-paper perforated with small holes should be
placed over the basin, as crepitation occurs on cooling.   If after the
first weighing a further drying is considered necessary, the perforated
cap should be put over the basin before it is placed in the oven, and
should not be removed until the moment before weighing; if this pre-
caution is not taken, a slight loss may occur.

The weight of magnesium oxide used must of course be subtracted
from the result.   The benzoic and cinnamic acids are part of the total
solids, and most important constituents of the tincture; they should
therefore be fixed by chemical means before drying.

A large batch of this tincture, made on the manufacturing scale, was
found to contain 19.4 grm. of extractive per 100 c.c. when tested by the
above method, using magnesium oxide as a fixing agent.   If the ex-
tractive from a compound tincture of benzoin is dried to a constant
weight at 100°, the results will be from 2% to 2.5% below the actual
amount of total solids present.

CINNAMIC BALSAMS.

Under this description are included Peruvian balsam, Tolu balsam,
and liquid storax.   These substances are all closely allied to one

another, but in their physical properties and quantitative chemical composition, they present considerable differences.

The following table exhibits the more important distinctions between Peru and Tolu balsams and storax:

	Peruvian balsam	Tolu balsam	Liquid storax
Botanical origin...	*Toluifera Pereiræ.*	*Toluifera Balsamum*	*Liquidambar orientalis.*
Geographical origin	San Salvador, Central America	Colombia, Turbace, Tolu, and Venezuela	Asia Minor.
Consistency and appearance........	Viscid, but not glutinous, dark brown liquid, resembling molasses; transparent and reddish-brown in thin layers Gradually thickens on exposure.	When fresh, yellow transparent, and liquid; changing rapidly to reddish-brown, and becoming solid and friable or brittle; but softening between the teeth, and readily fusing. Such samples have a granular crystalline structure; and crystals of cinnamic acid are visible under the microscope.	Brownish-yellow or greyish, viscous liquid. Under the microscope shows globules of water, tabular crystals of cinnamic acid, and frequently feathers of styracin.
Taste.............	Bitter and persistently irritating.	Sweetish, aromatic, and somewhat irritating.	Pungent and balsamic.
Odour...........	Agreeable.	Aromatic; more apparent on warming.	Sweetish or strong and oppressive.

The cinnamic balsams are closely allied, consisting essentially of the benzyl and cinnamyl esters of benzoic and cinnamic acids, mixed with resinous oxidation products of these esters, free benzoic and cinnamic acids, and the hydrocarbon cinnamene. The leading or characteristic constituents of Peru balsam may be said to be the cinnamein or benzyl cinnamate and styracin or cinnamyl cinnamate. Free benzyl alcohol is also present. In Tolu balsam, on the other hand, the proportion of resin is large; but of the esters benzyl benzoate predominates, and cinnamyl benzoate and cinnamate exist in but small proportions. In liquid storax of Mexican origin, phenylpropyl cinnamate exists in considerable quantity together with 2 isomeric alcohol-like substances called α- and β-storesinol, to which the formula $C_{36}H_{55}.(OH)_3$ is attributed (*Ber.*, 1876, **9**, 274), and the cinnamic esters of these substances.

In some cases the substances obtained from the cinnamic balsams have been decomposition products of the methods of analysis. The following method may be adopted for the recognition of the principal constituents of aromatic balsams: The substance is dissolved in 2 or 3 parts of ether, and filtered from any insoluble matter. The

solution is agitated with an equal volume of normal sodium hydroxide, the alkaline liquid withdrawn, and the agitation repeated with a fresh quantity of solution. If desired, the total acidity of the balsam can be deduced from the titration of an aliquot part of the alkaline liquid. The ethereal layer is then washed with water, and distilled at a gentle heat, the residue of neutral esters, etc., being weighed. The residue is then fractionally distilled.

The first fraction will contain any *cinnamene* which may be present, the next being rich in *benzyl alcohol*, which may be extracted by agitation with water and will yield benzaldehyde and benzoic acid by oxidation. *Cinnamyl alcohol* and *benzyl benzoate* pass over next, and at a higher temperature *benzyl cinnamate* and *cinnamyl benzoate* and *cinnamate* may be obtained. These esters suffer more or less decomposition unless the distillation is conducted *in vacuo*, and hence the last fractions consist largely of cinnamic acid, which can be removed by agitating the distillate with sodium carbonate solution. The alkaline liquid separated from the ethereal solution should be saturated with carbon dioxide, which precipitates much *resin*. The liquid is filtered, concentrated, and treated with hydrochloric acid, when a bulky precipitate is obtained representing the *free benzoic* and *cinnamic acids* of the balsam. These substances may be identified by their ordinary reactions. For their approximate separation, one half of the precipitate may be boiled with milk of lime and the liquid filtered and allowed to become cold, when the sparingly soluble calcium cinnamate is deposited in shining needles, the more soluble benzoate remaining in solution. The methods indicated on page 407 may also be utilised for the separation of the 2 acids. When an exact estimation of the free acids of a balsam is desired, it is better to agitate the ethereal solution with sodium carbonate instead of sodium hydroxide, as the latter reagent is liable to cause some decomposition of the esters.

Except for purposes of research, it is rarely necessary to make such an analysis of a balsam as is indicated above.

PERUVIAN BALSAM.

White Peru balsams have been described by Biltz (*Chem. Zeit.*, 1902, **26**, 436), Thoms and Biltz (*Zeit. Oesterr. Apoth. V.*, 1904, **42**, 943), and by Hartwich and Hellström (*Arch. Pharm.*, 1905, **243**, 218).

Peruvian balsam is readily soluble in all proportions in absolute alcohol, glacial acetic acid, chloroform, acetone, and ethyl acetate;

with an equal bulk of alcohol and ether it yields a clear solution, which on further addition of the solvent becomes turbid and deposits resin. Diluted alcohol takes up only a small proportion of the balsam. Cold ether and light petroleum dissolve it partially.

Cold light petroleum only dissolves the cinnamein and cinnamic acid of the balsam, but on employing the hot solvent styracin is also dissolved and is deposited in crystals on cooling. Carbon disulphide acts in a characteristic manner. Agitated with three times its weight of the cold solvent, the greater part of the balsam is dissolved to a colourless or slightly coloured liquid, from 10 to 16% remaining as a reddish-brown, sticky liquid, adhering firmly to the sides of the glass, whilst the solution may be readily poured off.

Analysis.—The investigations of Dieterich (*Anal. d. Harze.*, etc.) have shown that many of the commonly accepted tests for purity of this balsam have no value. He gives the following methods as of service:

Direct Acid Number.—1 grm. of the sample is dissolved in 200 c.c. of alcohol (96%) and titrated with decinormal alcoholic alkali, using phenolphthalein. The c.c. of alkali required multiplied by 5.616 gives the direct acid number.

Cold Saponification Number.—The procedure is mainly as given under "Benzoin," using 1 grm. of the sample in a 500 c.c. glass-stoppered flask with 50 c.c. of light petroleum (sp. gr. 0.700) and 50 c.c. half-normal alcoholic alkali. After standing 24 hours at room temperature, 300 c.c. of water is added, well shaken, until the separated dark alkali salt has been dissolved, and the solution titrated, with continuous agitation, with half-normal sulphuric acid in the presence of phenolphthalein. The c.c. of alkali neutralised by the sample, multiplied by 28.08, gives the cold saponification number.

The *ester number* is obtained by subtracting the direct acid number from the cold saponification number.

Ether Insoluble Matter.—This is obtained by Dieterich by adding warm ether in small portions to a weighed portion of the sample until a portion of the solvent no longer leaves any residue on evaporation. The undissolved portion is then weighed. It will probably be better to extract in a Soxhlet tube.

Aromatic and Volatile Ingredients.—The ethereal extract is shaken with 20 c.c. of a 2% sodium hydroxide solution, separated and evaporated at room temperature until no odour of ether is perceptible. The residue is placed for 12 hours in the desiccator, weighed, placed for

a second 12 hours in the same and weighed again. The mean between these 2 weights is taken as the datum for fixed matter from which the volatile matter can be calculated.

Esters of Resin-acids.—The alkaline solution separated from ether by the action of the alkali, as noted in the last paragraph, is rendered acid by dilute hydrochloric acid, filtered through a tared filter and washed by the aid of a filter pump with as little water as possible until the washings are free from chlorides. The residue dried at 80° to constant weight is taken.

With these processes, Dieterich obtained from commercial samples the following range of data:

Sp. gr...	1.135	1.145
Direct acid number.	60.0	80.0
Cold saponification number.	240.0	270.0
Ester number.	180.0	200.0
Resin esters.	20.0%	28.0%
Aromatic and volatile ingredients.	65.0%	77.0%
Ether insoluble.	1.5%	4.5%

From authentic pure specimens from Honduras the following figures were obtained:

	I	II	III
Direct acid number.	77.4	76.9	77.3
Cold saponification number.	241.0	214.3	215.0
Ester number.	165.6	137.4	137.6
Resin esters.	15.7%	13.2%	17.3%
Aromatic and volatile ingredients.	71.4%	77.5%	73.6%
Ether insoluble.	4.4%	4.3%	3.5%

The United States Pharmacopœia requires that Peru balsam shall have a sp. gr. between 1.140 and 1.150 at 25°, that when mixed with sodium hydroxide solution, one extraction with ether shall remove 56% of cinnamein, and that the latter shall require not less than 23.49% of potassium hydroxide for its saponification. According to the same authority, Peru balsam must contain not more than 14.69% of acid resins, calculated as cinnamic acid. The German Pharmacopœia regulation is satisfied if the 56% of cinnamein is obtained by three successive extractions with ether, but it must require at least 23.66% of potassium hydroxide for hydrolysis, and the balsam must have a cold saponification value not less than 224.6.

Adulterations of Peruvian Balsam.—Peruvian balsam is liable to adulteration with the cheaper cinnamic balsams (Tolu and storax); copaiba and gurjun balsams; colophony; an alcoholic solution or extract of gum benzoin; alcohol; and even with fixed oils, especially

castor oil.   Hence the examination of Peru balsam for the detection of these adulterants is of some importance.   Many of the usual adulterants of balsam have a lower sp. gr. than the genuine substance, which varies in density between very narrow limits, 1.150 being the maximum and 1.137 the extreme minimum.   Any sample having a lower density than 1.138 should be regarded with suspicion.

The presence of *alcohol* is indicated by the loss of volume undergone by the balsam on agitating with water.   Small quantities may be detected by distilling the sample with water and sodium carbonate and examining the distillate by the iodoform and chromic acid tests.

According to Rosenthaler (*Zeit. anal. Chem.*, 1905, **44,** 292), pure Peru balsam, when treated with a solution of vanillin in hydrochloric acid, gives no colouration, but if it is adulterated with 5% or more gurjun balsam, a purple-red and then a violet colour is produced, whilst in the presence of 10% of copaiba balsam the colour is faint violet.

K. Dieterich (*Ber. pharm. Ges.*, 1908, **18,** 135) states that adulteration with 30% of Tolu balsam can be detected by the following test: A small quantity of the balsam is dissolved in ether, and to the solution a little concentrated sulphuric acid is added to form a lower layer. Hydrochloric acid is then cautiously added so that 3 strata are formed. With genuine Peru balsam the upper and lower strata are red and the intermediate hydrochloric acid is colourless.   Tolu balsam imparts a very characteristic green colour to the upper ethereal layer.[1]

The artificial Peruvian balsam known as "Perugen," when shaken with 5 volumes of light petroleum and the extract evaporated, gives a residue, which when treated with a little nitric acid (sp. gr. 1.38) acquires an olive-green colour.   The residue from the natural balsam becomes golden-yellow when similarly treated.   (Cæsar and Loretz, *Pharm. J.*, 1905, [iv], **21,** 579.)

According to the United States Pharmacopœia, the light petroleum extract of Peru balsam, when shaken with an equal volume of copper acetate solution (1:1,000), should not become green or bluish-green (absence of resin, turpentine, storax, fatty oils, etc.).

The British Pharmacopœia requires that the balsam shall contain 40% of resin insoluble in carbon disulphide and that the solution in the latter solvent shall have only a slight fluorescence (absence of gurjun balsam).   When mixed with half its volume of lime and

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[1] Perrot and Goris, however, state that the pure Peru balsam gives this reaction.

heated on a water-bath for 30 minutes, it should not form a solid mass (absence of resin, storax, or copaiba balsam).

From his analyses of genuine and adulterated balsams, Dieterich concludes that adulterations usually raise the direct acid number and lower the cold saponification number.

A low ester-number indicates adulteration; if below 100 it suggests colophony, Tolu balsam, or benzoin.

The matter insoluble in ether has a sorting value, but is of no use in detecting common adulterations.

In commercial samples the proportion of cinnamein ranged from 65 to 75%, and of resin esters 20 to 28%; that is, a ratio of 1 of the latter to 3 of the former. Ratios, therefore, of 1 to 2 or 1 to 5 indicate much adulteration.

In valuing a sample, a high content of cinnamein is preferable to high content of resin esters.

TOLU BALSAM.

This is from a leguminous plant, *Myroxylon Toluifera*, growing in the northern portion of South America. In fresh condition the balsam is brownish-yellow, transparent in thin layers, and non-crystalline, but in time becomes hard, crystalline, and darker. The odour is aromatic and pungent. The m. p. ranges from 60° to 65°. It dissolves in alcohol, chloroform, and in watery solutions of alkalis. The alcoholic solution is acid to litmus.

The constituents of Tolu balsam are not fully known, but it appears to consist principally of the following ingredients:

(1) An oily portion, benzyl benzoate with a little benzyl cinnamate; (2) cinnamic and benzoic acids; (3) vanillin; (4) toluresinotannol benzoate and cinnamate. Of these (4) is the most abundant; (1) forms about 7%; (2) from 12 to 15%; (3) only traces. About 3% of impurities of various kinds are present.

By steam distillation on a large scale, a small amount of a volatile oil of pleasant odour can be obtained. This has a sp. gr. ranging from 0.945 to 1.090, slight optical activity, sometimes positive, sometimes negative, and contains phellandrene.

Analysis.—The assay of Tolu balsam usually includes the determination of the *direct acid number*, the *cold saponification number*, the *ester number*, the *matter soluble in ether*, the *volatile matter*, and the *esters of resin acids*, according to Dieterich's directions for Peru balsam.

The United States Pharmacopœia requires an acid number 111.4 to 167.2, whilst the German Pharmacopœia sets the limits at 112.3 to 168.4.

The following method of analysis is recommended by Delphin (*Svensk. Pharm. Tidskr.*, 1907, **3**, 415): 2 grm. of the sample are dissolved as completely as possible in 5 c.c. of ether contained in a separating funnel. To the solution 20 c.c. of ether and N-potassium hydroxide solution are added and the mixture carefully shaken. After separation the aqueous layer is run into a 75 c.c. flask, the ethereal liquid washed with 2 c.c. of water, and the washings added to the aqueous portion. The ethereal extract is transferred to a tared Erlenmeyer flask and evaporated on a water-bath. After heating the residue on the water-bath for 30 minutes it is exposed over sulphuric acid for 12 to 18 hours and weighed, this giving the cinnamein. The alkaline aqueous liquid is treated with sodium hydrogen carbonate (2 grm.) until an abundant yellowish-white precipitate is formed, and then the liquid is submitted to a stream of carbon dioxide for an hour. The solution is filtered, and the precipitate washed with warm water until the wash-water is no longer alkaline. For the estimation of the resin esters the precipitate is dried to constant weight. The filtrate from the resin esters is treated with 6–7 c.c. of 25% hydrochloric acid. After effervescence has ceased the resin acid is collected on a tared filter, washed with boiling water until the filtrate is free from acid, dried and weighed. The cooled filtrate, in which the cinnamic acid will have crystallised, is extracted first with 40 c.c., then with 20 c.c. of ether. The combined ethereal extracts are titrated with $N/10$ potassium hydroxide solution (1 c.c. corresponds to 0.0148 grm. of cinnamic acid) in the presence of phenolphthalein.

A good balsam should contain not less than 8% of cinnamein and 25% of cinnamic acid, nor more than 1% of resin acid.

Adulteration of Tolu Balsam.—The common adulterant is colophony, but when the balsam is high in price other substances (*e. g.*, copaiba) may be used.

For the detection of colophony qualitatively the Storch-Morawsky test (see under "Colophony") may be used.

The following test for colophony is described by Hirschsohn (*Pharm. Zeit. f. Russ.*, 1895, **34**, 497): The balsam is extracted with 4 to 5 volumes of light petroleum and the extract shaken with an equal volume of copper acetate solution. The production of a green colouration in

the petroleum layer indicates the presence of colophony. Perrot and Goris recommend a similar test (*Bull. Sci. Pharm.*, 1908, 636).

The solubility in carbon disulphide has been proposed as a test and in the British Pharmacopœia of 1898 is given as follows:

5 grm. of the sample are extracted with 25 c.c. and then 10 c.c. of warm carbon disulphide. Upon evaporating the mixed solutions, the residue should require not less than one-third of its weight of potassium hydroxide for saponification, thus indicating a sufficient amount of cinnamic and benzoic acids in the sample.

Some good authorities are, however, not inclined to rely on this test, and much further study of this balsam is needed. K. Dieterich says that little if any pure Tolu balsam is on the market. He gives the following data obtained by E. Dieterich, with which his own figures correspond, but the latter are not specially quoted:

Direct acid number........................ 114.8–158.6
Saponification number..................... 155.3–187.4
Ester number............................. 31.2–40.5

Solubility:

Alcohol (90%)........................ ....wholly soluble.
Ethyl acetate............................wholly soluble.
Chloroform.......................almost wholly soluble.
Ether............................... 53.2–87.9%
Benzene........................ 82.2–nearly 100%
Petroleum spirit......................... 2.2–10.2%
Oil of turpentine........................ 27.8–54.5%
Carbon disulphide....................... 19.6–88.1%

Syrup of Tolu Balsam.—Commercial syrup of Tolu balsam is prepared either (1) by the British Pharmacopœia official method; (2) by precipitating an alcoholic tincture, or (3) by admixture with a distillate of the balsam.

According to Astruc and Cambe (*J. Pharm. Chim.*, 1903, [vi], **17**, 367), only the syrup prepared by the official direct maceration method liberates iodine from potassium iodide solution. Both the official syrup and that prepared from the tincture give a marked yellowish-green colour in the presence of excess of alkali. But the preparation from the distillate of Tolu balsam gives neither of these reactions.

LIQUID STORAX.

This is the product of *Liquidambar orientalis* of Asia Minor, and of *Liquidambar Styraciflua* of America. It is a brownish-yellow or

greyish viscous liquid, the better qualities of which possess a sweet, vanilla-like odour. Inferior specimens contain impurities which render the odour oppressive and disagreeable.

The taste is pungent and balsamic. Under the microscope globules of water and crystals of cinnamic acid and styracin are visible.

Oriental storax (from *Liquidambar orientalis*) contains styrene, $C_6H_5.CH:CH_2$, cinnamic acid, styracin (cinnamyl cinnamate), $C_9H_9C_{91}H_7O_2$), phenyl-propyl cinnamate, ethyl cinnamate, vanillin, ethyl-vanillin; α- and β-storesin, $C_{35}H_{55}(OH)_3$, an amorphous resin, traces of benzoic acid and storesinol cinnamate. According to Tschirch, benzoic and cinnamic acids are never found in the same specimen of oriental storax.

Storesinol has the formula $C_{16}H_{25}O(OH)$, and its cinnamic ester is present to the extent of about 35% in the balsam.

American storax is known also as *sweet gum*, and, according to Harrison and Maisch (*Arch. Pharm.*, 1875, **206, 5**45), it is identical with oriental storax; but this is improbable. It contains styracin, phenyl-propyl cinnamate and storesin; but not ethyl or benzyl cinnamate. Styrene and traces of vanillin are probably present.

Qualitative Tests.—When treated with strong alcohol, ether, or chloroform, liquid storax dissolves, but generally leaves some mechanical impurities. With an equal weight of warm alcohol it yields a turbid solution of acid reaction. The filtered liquid, when evaporated, yields not less than 70% of the original balsam, as a brown semisolid mass which constitutes "prepared storax." This is entirely soluble in ether and carbon disulphide and almost completely soluble in benzene, but is only partially soluble in cold petroleum spirit, more freely in hot petroleum spirit, and the solution deposits crystals of cinnamic acid and styracin on cooling.

The residual pressings of the bark after obtaining the liquid storax are used under the name "*styrax calamitus.*" Mixtures of storax with an inert solid are also known by the name, and formerly the resin of *Styrax officinalis* was also known in commerce under this description.

Analysis.—K. Dieterich recommends the following process for the assay of liquid storax (*Pharm. Centr. Halle*, 1899, **40,** 423). Water is estimated by drying 2 grm. at 100° to constant weight. The residue is ignited and the ash weighed. To determine the part soluble in alcohol, 10 grm. are weighed into a 200 c.c. beaker and dissolved in 100 c.c. of 96% alcohol by gentle warming. The liquid is filtered

through a tared filter and the residue washed with 50 c.c. of hot alcohol. The filtrate and washings are collected in a tared porcelain basin and evaporated to dryness. In order to prevent creeping, it is best to float the basin on water contained in another basin which is heated on a water-bath. It is advisable to weigh with the basin a small glass rod with which the residue is stirred in order to facilitate drying. The latter is carried out at 100° until the weight is constant. The residue on the filter, dried at 100°, gives the part insoluble in alcohol.

The direct acid number is determined by dissolving 1 grm. of the storax in 100 c.c. of 96% alcohol and titrating the solution with $N/2$ alcoholic potassium hydroxide, using phenolphthalein as indicator. The number of c.c. required, multiplied by 28.08, gives the direct acid number.

The procedure for the determination of the saponification number is the same as that given under Benzoin.

Storax should contain not more than 30% of water nor more than 1% of ash. The United States Pharmacopœia requires at least 60% to be soluble in alcohol and the residue to be soluble in ether and carbon disulphide. Not more than 3% should be insoluble in alcohol (the German Pharmacopœia fixes the standard at 2.5%), the acid number should lie between 55 and 75, and the cold saponification number between 100 and 140.

The commoner adulterants of storax are turpentine rosin, castor oil, olive oil, and similar fatty oils. Ladanum resin has been found by K. Dieterich.

Samples of crude storax have been examined chiefly by continental chemists, and the following figures, compiled from their results, represent a wide scope:

	Acid number	Ester number	Saponification number
Beckurts and Brüche[1]	68–93	112–153	180–222
A. Kremel[2]	47.6	31.9	79.5
E. Dieterich	37.2–96.7	74.6–168	134.6–249
K. Dieterich[3]	57.5–59.4	....	....
Evers	52.2–56.7	173.5–184.2	230.2–236.4

[1] 6 samples of authentic origin.
[2] A sample adulterated with turpentine.
[3] 2 pure samples.

K. Dieterich has further examined a number of commercial and absolutely authentic samples, and gives the following comparative results:

	Authentic	Commercial
Water, ...	26.21– 40.97%	19.58– 31.95%
Ash...........................	0.5 – 0.92%	0.24– 3.64%
Soluble in alcohol (after deducting water)	57.14– 65.49%	64.90– 77.17%
Acid number....................	59.38– 70.70	38.22– 72.29
Ester number..................	35.42– 74.43	47.81–110.03
Saponification number...........	104.67–135.36	111.89–187.76

E. Dieterich gives the following table of solubilities:

	%
90% alcohol...	56.14–84.00
Acetic ether...	69.40–73.60
Chloroform...	69.20–72.60
Ether..	65.80–82.80
Benzene..	64.80–74.80
Turpentine...	54.40–57.80
Carbon disulphide......................................	62.30–67.80
Light petroleum..	15.00–19.40

The sp. gr. should lie between 1.113 and 1.121, according to Beckurts and Brüche, who also give the amount dissolved in an equal volume of pure alcohol as 61 to 71%.

The following interesting table is given by K. Dieterich. Unfortunately, the figures for the pure storax are not given:

Pure storax with	Water, %	Ash, %	Soluble in alcohol (after deducting water). %	Acid No.	Ester No.	Saponification No.
20% olive oil....	33.73	0.62	63.87	53.65	72.98	126.63
30% olive oil....	28.22	0.47	70.59	53.08	78.34	131.42
20% castor oil...	33.96	0.51	64.72	57.21	66.84	124.05
30% castor oil...	29.30	0.33	69.65	51.31	79.88	131.19
20% turpentine..	39.56	0.61	59.30	78.40	29.53	107.93
30% turpentine..	34.62	0.53	63.36	84.40	23.01	107.05

Soluble in light petroleum.................. 37.54–58.96%
Soluble in alcohol 90%..................... practically entirely
Soluble in ether........................... 93.14–100%
Soluble in chloroform...................... almost entirely
Soluble in acetic ether.................... entirely
Soluble in benzene........................ 95.75–100%
Soluble in turpentine..................... 81.8 –99.55%
Soluble in carbon disulphide.............. 86.8 –93.39%

The British Pharmacopœia (1898) only recognises "*Styrax Præparatus*," the product of *Liquidambar orientalis*, purified by solution in alcohol, filtration, and evaporation of the solvent. This authority requires it to give off no moisture on heating and to evolve an odour of essential oil of bitter almonds when boiled with sulphuric acid and a solution of potassium dichromate.

Resinous Adulterants in Storax.—Ahrens and Hett (*Zeit. ang. Chem.*, 1903, **16,** 384; also *Pharm. J.*, 1904, [iv], **19,** 547) find that storax adulterated with rosin yields to light petroleum from 55.1 to 63.7% of extract; this has an acid value between 116.3 and 120.9, and a cold saponification value between 171.6 and 177.6. Specimens of pure storax of recent and older importation gave a light petroleum extract of 37.6 to 47.6% with an acid value ranging from 36.6 to 62.9 and a saponification value (cold) of 194.6 to 198.4. Adulteration with rosin is more readily detected by this method of separating and treating the light petroleum spirit extract than by determining the saponification constants of the original drug, as recommended by Dieterich.

SALICYLIC ACID AND ITS ALLIES.

Salicylic acid is the type of a group of compounds containing the radical hydroxyphenyl, $C_6H_4(OH)$, and has itself the constitution of a hydroxyphenyl-carboxylic acid, $C_6H_4(OH).COOH$. Thus it may be regarded as a hydroxy-benzoic acid, and as the hydroxyl and carboxyl groups occupy adjacent positions in the benzene-nucleus, salicylic acid is the *ortho-* form of the acid, all 3 modifications of which are known. The fact that 2 of the hydrogen atoms of the benzene-nucleus are replaced, renders all the compounds of the group capable of existing in ortho-, meta-, and para-modifications. In the case of the homologues of the hydroxybenzoic acids, where a third substitution of hydrogen by methyl or other alkyl-radical occurs, the number of possible isomerides is still further increased.

Isomeric Hydroxybenzoic Acids.

Salicylic acid and methyl salicylate occur in many plants. *p*-Hydroxybenzoic acid has been found in the pods of *Bignonia catalpa*.

The following table exhibits the leading differences between the 3 isomeric hydroxybenzoic acids:

	Ortho-acid (salicylic acid)	Meta-acid	Para-acid
Formula.....................	$C_6H_4 < {}^{OH(1)}_{COOH(2)}$	$C_6H_4 < {}^{OH(1)}_{COOH(3)}$	$C_6H_4 < {}^{OH(1)}_{COOH(4)}$
Sp. gr. at 4° (Schröder).........	1.4835	1.473	1.468
M. p................................	156.7°	200°[2]	213°–214°
Solubility:			
In water at 0°...............	1 in 1,100.[1]	1 in 265.	1 in 580.
In water at 15° to 18°........	1 in 1,000.	1 in 108.	1 in 126
In chloroform...............	Readily soluble.	Almost insoluble.	Very slightly soluble.
Reaction with ferric chloride....	Deep violet colour.	No change.	Yellow flocc. ppt. sol. in excess.
Reaction when heated in a current of dry ammonia gas........	Yields phenol, CO_2, etc.	Yields hydroxy-benzonitrile, $C_6H_4(OH)CN$, melting at 82°.	Yields phenol, CO_2, etc.
Products with bromine water in excess.....................	$C_6H_2Br_3.OBr + CO_2$.	$C_6HBr_3(OBr).COOH$.	$C_6H_2Br_3.OBr + CO_2$.
Antiseptic properties...........	Strong.	None.	Doubtful.

SALICYLIC ACID. O-HYDROXYBENZOIC ACID.

$$C_7H_6O_3;\ or,\ C_6H_4 < {}^{OH}_{CO_2H}$$
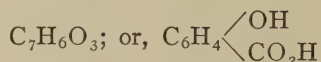
Salicylic acid is the only modification of the 3 isomeric hydroxy-benzoic acids of any importance.

Salicylic acid and methyl salicylate occur in a number of plants and small quantities have been found in certain fruits, thus it has been detected by Jablin-Gonnet (*Ann. Chim. anal.*, 1903, **8**, 371) in wild cherries, by Suss (*Verh. Vers. deutsch Naturf. Aertze*, 1902, ii, 102), and Portes and Desmoulières (*J. Pharm. Chim.*, 1901, [vi], **14**, 342) in strawberries, and by Utz (*Oesterr. Chem., Zeit.*, 1903, **6**, 385), and Windisch (*Zeit. Nahr. Genussm.*, 1903, **6**, 447) in both strawberries and raspberries.

Salicylic acid was originally prepared from salicin (Piria, *Annalen*, 1839, **30**, 165). The so-called "natural" acid, prepared from oil of wintergreen (*Gaultheria procumbens*) or oil of sweet birch (*Betula lenta*), was first obtained by Cahours (*Annalen*, 1843, **48**, 60). Although far more expensive than the artificial product, the natural acid has the advantage of being free from *p*-hydroxybenzoic acid, which is by no means harmless in its physiological effects.

[1] According to Bourgoin (*J. Pharm. Chim.*, 1879, [iv], **30**, 488), the solubility of salicylic acid at 0° is 1 part in 666, instead of the number given in the text, which is due to Ost (*J. pr. Chem.*, 1878, [ii], **17**, 228).
[2] Kellas (*Zeitsch. physikal. Chem.*, 1897, **24**, 223) gives 188°.

Practically the whole of the acid of commerce is now prepared by the method of Kolbe and Lautemann (*Annalen*, 1860, **115,** 157), which is based on the action of carbon dioxide on sodium phenoxide.

When potassium phenoxide is heated in a stream of carbon dioxide, it is acted on in a manner similar to sodium phenoxide in Kolbe's process, yielding pure di-potassium salicylate up to 150°; but above that temperature the isomeric *p*-hydroxybenzoate is also produced, and at 220° is the sole product.[1]   The same substance is formed if the alkali employed in Kolbe's process contains potassium hydroxide, and, according to B. Fischer, it is also produced if the temperature be too low when the gas is passed.   Too high a temperature is said by Fischer to cause hydroxy-*iso*phthalic acid to be formed at that stage, owing to the action of the gas on the sodium salicylate already formed.   In a well-conducted operation, *p*-hydroxybenzoic and hydroxy-*iso*phthalic acids are not usually formed in quantities exceeding 0.4%, and the former may be easily removed by washing, as it is readily soluble in water.   Hydroxy-*iso*phthalic acid is less soluble, and may be present to the extent of 1% in some cases.[2]

If traces of iron compounds are present in the materials used in Kolbe's process, brown or yellow oxidation products are formed which are insoluble in water, and give a yellow colour to the salicylic acid obtained.

Salicylic acid crystallises from alcohol in large monoclinic prisms. As met with in commerce, the acid usually occurs as a granular powder, consisting of minute, broken, acicular crystals.   It has a sweetish, acidulous, acrid taste.   The sp. gr. is 1.483 at 4°.

The m. p. of salicylic acid has been stated by various observers at points ranging from 155° to 159°, but Fischer finds the m. p. of the pure acid to be 156.75° (corrected), and this result has been confirmed by Dunstan and Bloch (*Pharm. J. Trans.*, 1890, [iii], **21,** 429).   Even a

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[1] Mono-potassium salicylate is converted into the basic *p*-hydroxybenzoate and phenol when heated to 220°, whereas the corresponding sodium salt yields the *o*-hydroxybenzoate or salicylate, together with phenol.

[2] HYDROXY-*iso*PHTHALIC ACID, $C_6H_3(COOH)^1(COOH)^3(OH)^4$, is now rarely met with in commercial salicylic acid.   It may be detected by distilling the suspected sample in a current of steam, when it remains in the still in the form of a light grey powder or small lumps.   By dissolving it in hydrochloric acid and filtering the solution through charcoal, the acid may be obtained in slender white needles melting with decomposition at 305° to 306°.

HYDROXY-NAPHTHOIC ACID, $C_{10}H_6(OH).COOH$, is a substance which bears the same relation to naphthalene that salicylic acid bears to benzene.   It is produced by the action of carbon dioxide on perfectly dry sodium α-napthol at 130°.   It forms colourless acicular crystals melting at 185° and requiring 30,000 parts of cold water for solution.   Its salts give a blue colouration with ferric chloride.   The corresponding acid from β-naphthol melts at 235° and gives a violet-black colour with ferric chloride.   Both varieties of hydroxynaphthoic acid are said to be powerful antiseptics, retarding the putrefaction of blood and urine much more perfectly than salicylic acid (*Pharm. J.*, 1887, [iii], **18,** 537, 823).

small proportion of the cresotic acids tends to lower the m. p. of the sample.

When gradually heated to about 200°, salicylic acid sublimes in slender shining needles, but when heated rapidly in admixture with powdered glass or sand, it is resolved into phenol and carbon dioxide. Salicylic acid distils readily in a current of steam at 60 to 80 pounds pressure, and even vaporises on boiling its aqueous solution.

Salicylic acid is very sparingly soluble in cold water, and only moderately soluble in boiling water. The determinations of its solubility by different observers vary greatly. According to the British Pharmacopœia (1898), the acid is soluble in about 550 parts of cold or 9 of boiling water, in 3.5 of alcohol of 90% strength, in 2 parts of ether, in 55 of chloroform, and in 195 parts of glycerin. It is also readily soluble in carbon disulphide, and is dissolved by 80 parts of benzene. Salicylic acid may be conveniently crystallised from hot light petroleum. Agitation with ether, chloroform, or carbon disulphide readily removes salicylic acid from its aqueous solutions. H. Taffe recommends a mixture of ether and light petroleum for this purpose.

The solubility of salicylic acid in cold water is greatly increased by the presence of various salts.[1]

When ingested, salicylic acid is eliminated by the kidneys, partly in an unchanged state and partly in the form of the so-called *salicyluric acid*, a body which really has the constitution of *salicyl-glycocoll* $[C_6H_4(OH)CO].NH.CH_2.COOH$. This compound crystallises in fine needles, m. p., 160°, which are slightly soluble in water, but readily in alcohol. It gives a violet colouration with ferric chloride. The barium salt forms prisms very slightly soluble in water. When heated with concentrated hydrochloric acid, salicyluric acid is hydrolysed to salicylic acid and glycocoll (amino-acetic acid).

Salicylic acid and its salts and esters are used extensively in medicine, especially as intestinal antiseptics and in the treatment of gout and rheumatism of the joints.

Salicylic acid and its derivatives are now extensively employed as domestic remedies without seeking medical advice, but the practice

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[1] Mixed with 1 part potassium nitrate, it dissolves in 50 parts of cold water.
Mixed with 1.5 parts ammonium citrate, it dissolves in 60 parts of cold water.
Mixed with 2 parts sodium sulphite, it dissolves in 50 parts of cold water.
Mixed with 2 parts sodium phosphate, it dissolves in 50 parts of cold water.
Mixed with 2.5 parts sodium phosphate, it dissolves in 12.5 parts of cold water.
Salicylic acid is very soluble in solutions of borax, a compound of the formula $Na(BO)2C_7H_5O_3$ being said to be formed. The liquid, which is stated to be more powerfully antiseptic than either of its components, soon undergoes decomposition.

is not free from danger. Salicylic acid, even when pure, has distinct toxic properties, and its salts cause albuminuria. The free acid, dissolved in flexible collodion or in the form of ointment, is strongly caustic and is employed as a corn solvent.

Salicylic acid now finds an extensive application as a preservative of various articles of food, though its use for such purposes is strictly prohibited in France, the United States, and some other countries.[1] Wine, beer, milk, lime- and lemon-juice, temperance beverages, and many other articles are treated with salicylic acid in quantities which are often largely in excess of those necessary to preserve them. Such a practice is strongly to be deprecated, as the habitual and unconscious ingestion of an antiseptic necessarily tends to impair the digestive processes.

The employment of salicylic acid for preserving milk is now far less common than the use of formalin or boric acid for that purpose. Wines and temperance beverages frequently contain considerable quantities of salicylic acid,[2] and it is also extensively used in jam-making, from 4 to 8 grains of the acid to the pound being sufficient to prevent fermentation indefinitely. Uncooked fruits, such as cherries, plums, etc., may be preserved by pressing them, treating every pound of the juice with 15 grains of salicylic acid, heating the juice, and after cooling adding it to the pressed fruit.

For a very detailed study of the influence of salicylic acid on digestion and health, see *Bull.* 84, Part II (1906), of the U. S. Dept. of Agriculture, Bu. of Chem.

The addition of 1 grm. of salicylic acid to the litre preserves a 10% solution of tartaric acid perfectly; but a solution of citric acid of the same strength requires twice that amount. Salicylic acid is stated not to have a preserving action on a solution of sodium succinate.

When an aqueous solution of salicylic acid is kept for some time,

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[1] A Departmental Committee on Food Preservatives appointed in 1899 recommended that salicylic acid should not be used in greater proportion than one grain per pint in liquid food and one grain per pound in solid food, and that its presence should in all cases be declared; also that salicylic acid, in common with all other preservatives, should be prohibited in milk and in all dietetic preparations intended for invalids and infants (*Analyst,* 1901, 26, 332). These recommendations resulted in 1906 in the issue of a circular by the Local Government Board (England) urging the desirability of prosecutions being instituted against vendors of "preserved" milk, and stating that milk may be presumed to have been rendered injurious to health if found to contain more than 1 part of formaldehyde, or 57 parts of boric acid, per 100,000 parts.

[2] According to medical witnesses called to defend the use of salicylic acid for this purpose, its addition is absolutely necessary to preserve the wine, and cannot possibly be injurious to health. This evidence was given at the hearing of a summons at Liverpool (October, 1900) for selling ginger wine containing 13 grains of salicylic acid to the pint. The analyst stated that of 33 samples of ginger wine examined by him, none of the others contained more than 4 grains per pint. A member of the defendant's firm deposed that they had tried smaller quantities of salicylic acid as a preservative, but found that the wine went bad.

a fungoid growth forms, and this gradually decomposes all the salicylic acid (F. E. Lott, *J. Soc. Chem. Ind.*, 1903, **22**, 198). The rate of decomposition was found to be increased by the addition of small amounts of ferric chloride, thus confirming the statement that the growth of many moulds is stimulated by dilute iron solutions.

COMMERCIAL SALICYLIC ACID.

As now met with in commerce, salicylic acid, though varying much in quality, is free from those gross sophistications which are alleged to have occurred in the past.[1]

3 distinct grades of salicylic acid are now recognised in commerce, namely: ordinary acid, which is the cheapest; natural acid, which is the most expensive; and the so-called "physiologically-pure acid," which is intermediate in price. This last variety is a highly purified synthetical acid, free from any admixture of *p*-cresotic acid. Much of the ordinary salicylic acid of commerce is now of very considerable purity, and is very generally employed in medicine.

The facile formation of definite crystals is a useful indication of the purity of salicylic acid, the presence of foreign matters in its solutions greatly interfering with its crystallisation. Thus the presence of 5% of *p*-cresotic acid prevents the formation of large crystals, but 2% produces no material effect.

When agitated with cold concentrated sulphuric acid, salicylic acid should yield a perfectly colourless solution.

H. Kolbe (*J. pr. Chem.*, 1876, [ii], **14**, 143) gives the following method of testing the purity of salicylic acid: 0.5 grm. of the sample is dissolved in 5 or 6 c.c. of strong alcohol, the clear solution poured on to a watch-glass, and allowed it to evaporate spontaneously. The residual salicylic acid forms a ring of beautifully aggregated efflorescent crystals round the edge of the watch-glass. This mass is pure white if the acid tested be pure and recrystallised, but yellowish or yellow if the simply precipitated acid be used. If the colour be brownish or brown, the sample is unfit for internal use.

According to the British Pharmacopœia (1898), if salicylic acid be shaken up with a small proportion of water, the mixture filtered, and

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[1] Besides containing more or less sodium chloride, phenol, cresotic acid, and the isomerides of salicylic acid as natural impurities, salicylic acid adulterated with potassium sulphate, gypsum, starch, sugar, etc., is said to have been met with in America. Mineral adulterants would be left on igniting the sample, and starch and sugar detected by their insolubility in ether.

the filtrate evaporated, the residue should be white, and have no buff-coloured fringe. The absence of this fringe is stated to prove the absence of iron, colouring matters, and (erroneously) organic impurities.

Phenol is liable to be present in salicylic acid which has been sublimed. It may be detected by nearly neutralising the sample with sodium carbonate, and agitating the liquid with ether. On gently evaporating the ethereal liquid, the phenol may be recognised by its odour, taste, and chemical reactions.

It is stated by Carletti (Boll. Chim. farm., 1907, 46, 421) that as little as 0.02% of phenol in salicylic acid can be detected in the following way: 0.25 grm. of the sample is triturated in a mortar with 5 c.c. of water and the mixture poured into a test-tube. Two drops of an alcoholic solution of furfuraldehyde (2%) are then added, the liquid gently shaken, and 2 to 3 c.c. of concentrated sulphuric acid poured carefully to the bottom of the tube. In the presence of phenol a yellow ring is formed at the junction of the 2 liquids, above which a dark blue ring subsequently appears with a rapidity depending on the amount of phenol present.

p-Hydroxybenzoic acid, which is the isomeride most likely to be present in commercial salicylic acid, may be separated by drying the acid at 60° and agitating with anhydrous chloroform. Salicylic acid dissolves readily, but p- and m-hydroxybenzoic acids remain largely undissolved.

From benzoic acid, p-hydroxybenzoic acid may be separated by treatment with carbon disulphide, in which the latter acid is nearly insoluble.

Whilst salicylic acid is volatile in a current of steam, the isomeric hydroxybenzoic acids are not volatile, and hence remain in the retort together with hydroxy-isophthalic acid, if present. The last-named compound is now rarely met with in commercial salicylic acid. The cresotic acids behave like salicylic acid.

Commercial salicylic acid[1] formerly contained a considerable proportion of the allied acids. Thus J. Williams (Pharm. J. Trans., 1877, [iii], 8, 785) isolated from 15 to 20% of these acid impurities, but did not identify them, and Ewell and Prescott (Pharm. J. Trans., 1889, [iii], 19, 328) found still larger proportions. In 1890, Dunstan and Bloch (Pharm. J., 1890, [iii], 21, 431) further examined the specimens pre-

[1] Salicylic acid guaranteed to have been made from oil of wintergreen has been occasionally found to contain appreciable quantities of cresotic acid. This was in some cases due to the fact that the oil of wintergreen from which the acid had been made was nothing more than an artificial oil made in the first instance from artificial salicylic acid, the original impurities of which had been preserved during the various processes.

pared by Williams (which had been preserved in the museum of the Pharmaceutical Society of Great Britain), and showed that they were isomeric modifications of cresotic acid, homologous with salicylic acid (see page 509).

According to M. Charteris (*Pharm. J.*, 1890, [iii], **21**, 434), it is to the presence of cresotic acid in artificial salicylic acid that the objectionable symptoms (*e. g.*, delirium, restlessness, etc.) sometimes caused by the latter are attributable, and he states that when the impurity is removed the purified product has therapeutic characters identical with those of the natural acid.[1]

Formerly, commercial salicylic acid was liable to contain all 3 modifications of cresotic acid, but now a small proportion of the *p*-cresotic acid only is likely to be present.

The solubility of salicylic acid in boiling water is materially increased by the presence of cresotic acid. If, to a solution of the sample in boiling water, about 0.2 of its volume of alcohol be added and the liquid allowed to cool, pure salicylic acid will form separate, distinct, non-coherent crystals; whereas samples containing a notable proportion of cresotic acid form a network or woolly mass of small or indistinct crystals.

Pure salicylic acid melts sharply between 156° and 157°, but a very small percentage of *p*-cresotic acid materially reduces the m. p. of the sample and causes it to soften at a temperature below that requisite to produce actual fusion.[2]

To detect cresotic acid in salicylic acid, B. Fischer (*Pharm. Zeit. f. Russ.*, 1889, **28**, 378) recommends the following test: Calcium carbonate (1 to 2 grm.) is boiled with 15 c.c. of water in a 200 c.c. flask, and 3 grm. of the sample of salicylic acid added. The flask is shaken over a flame till the volume of the contents is reduced to 5 c.c., by which time some crystals will have formed. The liquid is cooled, the crystals separated, and the mother liquor transferred to a test-tube and evaporated to about 1 c.c. On rubbing the tube containing this concentrated liquid with a glass rod, crystallisation sets in. 1 c.c. of water is then added and the liquid is filtered through a plug of cotton-

[1] In 1890, shortly after the first publication of these researches (*Brit. Med. Jour.*, Nov. 30, 1889), a prosecution under the Sale of Food and Drugs Acts was instituted in Glasgow for selling salicylic acid containing 2.5% of cresotic acid (*Pharm. J.*, 1890, [iii], **21**, 394).
[2] "One can now obtain commercially an acid *physiologically pure*, even the last fraction of which has a m. p. of 156.85°; commercial *crysals* with a m. p. of 156.5° to 156.75°, containing about 0.05% impurity, the last 10% giving a m. p. 0.5° below the maximum; commercial *powder* with an initial m. p. of 156.4°, rising to 156.75°, containing 0.1% impurity, the last 10% giving a m. p. 1° below the maximum."—Squire's *Companion to the Pharmacopœia*, 1899.

wool. The filtrate is made up to 1 c.c. and a few drops of hydrochloric acid are added. If the sample contained as much as 3 to 5% of cresotic acid, a mixture of acids separates which fuses in boiling water and collects in thick oily drops at the bottom of the tube. This test is said to succeed only when the amount of cresotic acid exceeds 1%.

According to Engelhardt and Jones (*Amer. Pharm. Assoc. Drugg. Circ.*, 1908, **52,** 464), cresotic acids can be detected by Carletti's test (page 471) 0. 20 to 0. 15% of *o*-cresotic acid gives a brown colour zone, whilst with traces of phenol or *m*- or *p*-cresotic acid a faint violet colour is obtained.

The estimation of cresotic acid when in admixture with salicylic acid, if present in sufficiently large proportion, may be effected by careful titration of the sample with sodium hydroxide and phenolphthalein, as recommended by Ewell and Prescott (*Pharm. Record,* 1888; *Analyst*, 1888, **13,** 208). B. Fischer (*loc. cit.*) recommends with reason the replacement of the soda solution by decinormal baryta, which latter solution is necessarily free from carbonate. Fischer points out that the cresotic acid may be seriously overestimated, unless other impurites, such as moisture, colouring-matter, and sodium chloride, be previously removed. For this purpose he recommends that the sample be dissolved in ether, and the solution filtered from any insoluble matter. The filtrate is then evaporated at a gentle heat, and the residue dried at 60°, and finally over strong sulphuric acid. When the impurity is simply water it is perhaps preferable to treat the sample with light petroleum, agitate the solution with plaster of Paris, filter and evaporate to dryness.

In carrying out the operation, about 0. 2 grm. of the purified sample, weighed with the greatest possible accuracy and dried as already described at or below 60°, is treated with a few drops of an alcoholic solution of phenolphthalein, and, without adding water for solution, a centinormal solution of baryta added from a burette, with constant agitation, until the point of neutrality is approached. The flask is then rapidly warmed over a flame whilst the contents are kept in agitation, avoiding actual boiling until the remainder of the acid is dissolved, when the titration is completed. The baryta is preferably standardised against salicylic acid of known purity.

When pure salicylic acid is treated in the above manner, 1 grm. requires 724. 4 c.c. of centinormal baryta for its neutralisation, whereas an equal weight of one of the modifications of cresotic acid will neu-

tralise only 657.6 c.c.   Hence the difference, 66.8 c.c., represents the whole distinction between the 2 acids, so that the presence of each 1% of cresotic acid will lower the volume of centinormal alkali required for 1 grm. by 0.668 c.c.   Working on 0.2 grm. of the sample, this difference is reduced to 0.134 c.c.   Hence extreme care in operating is essential.

Ewell and Prescott (*Pharm. Record.*, 1888; *Analyst*, 1888, **13,** 237) have proposed a method of estimating cresotic acids in admixture with salicylic acid based on their conversion into the corresponding cresols on distillation with lime.   They direct that 15 grm. of the sample of acid and an equal weight of lime should be thoroughly dried and well triturated, together with an equal quantity of dry iron filings, and the mixture heated strongly in a glass retort, the distillate being collected in a well-cooled receiver.   The distillate is treated with just sufficient water to liquefy it, and the liquid mixed with an equal volume of 9% sodium hydroxide solution.   To this solution cold water is then added gradually until precipitation commences. From the volume of water required to cause precipitation the proportion of cresotic acid present in the sample is found by the following table:

Volumes of water required to precipitate mixed soda and distillate	Percentage of cresol in distillate	Percentage of cresotic acid in sample
6.7	5	4.9
6.0	10	9.8
5.25	15	14.8
4.5	20	19.8
4.0	25	24.7
3.6	30	29.7
3.3	35	34.7
3.1	40	39.7
2.8	45	44.7
2.6	50	49.7

It is evident that such a method as the foregoing can only be roughly approximate, and is useless when the proportion of cresotic acid is very small.

In this case it is better to neutralise a fairly large quantity of the sample with calcium carbonate (mixed with boiling water) and to filter the liquid.   The sparingly soluble calcium salicylate, which is

deposited on cooling, is filtered off, dried, and weighed.[1] The acid remaining in solution (of which the weight is determined by difference) is precipitated with hydrochloric acid, washed, dried, and a sample analysed by one of the above methods.

Reactions and Detection of Salicylic Acid.—When salicylic acid is heated to 195° to 220° it is, according to Graebe and Eichengrün (*Annalen*, 1892, **269**, 323), to a great extent converted into phenyl salicylate, and if the product is distilled, a considerable quantity of xanthone is formed. On the other hand, if *p*-hydroxybenzoic acid is heated in an open dish to 200°, phenol and carbon dioxide are the chief products, and there finally remains only a very small quantity of some compound of high m. p. *m*-Hydroxybenzoic acid undergoes very little change even on prolonged heating at 210°.

Concentrated sulphuric acid dissolves pure salicylic acid without colour, forming a sulphonic acid. Impure salicylic acid gives a yellowish-brown colouration.

By the action of cold concentrated nitric acid on salicylic acid nitrosalicylic acid is formed, but with fuming nitric acid picric acid results.

Bromine gives a reaction with salicylic acid indistinguishable from that produced by phenol, and the same is true of its behaviour with Millon's reagent.

Silver nitrate and lead acetate give white precipitates with neutral salicylates, but not with free salicylic acid. Salicylic acid is not precipitated by barium or calcium chlorides, and neutral salicylates only in strong solution. Neutral salicylates in not too dilute solution (1%) give a yellowish-brown precipitate with a solution of uranium acetate. When boiled with excess of baryta water, salicylic acid is precipitated as a basic barium salt.

With a solution of cupric sulphate, salicylates and free salicylic acid give an emerald-green colouration, visible in 2,000 parts of water and destroyed by ammonia or acids.

Salicylic acid prevents the precipitation of cupric salts by alkalis, but its isomerides have not this property.

The solution of salicylic acid in 2 molecules of sodium hydroxide prevents the precipitation of $1/2 CuO$ by addition of further alkali.

Fehling's solution is reduced by salicylic acid, and under favourable circumstances may be employed for its estimation.

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[1] If excess of milk of lime be substituted for calcium carbonate, a sparingly soluble basic calcium cresotate is formed, which cannot be separated from the salicylate.

On heating salicylic acid or one of its salts with methyl alcohol and sulphuric acid, methyl salicylate is formed, having an agreeable aromatic odour.

Salicylic acid, by virtue of its phenolic nature, combines with formaldehyde. On dissolving the acid in a little formaldehyde solution, evaporating the liquid nearly to dryness, and then adding strong sulphuric acid a compound is precipitated which is at first practically colourless, but becomes red, whilst the solution acquires a magenta colour.

Jorissen has observed that when a solution of salicylic acid or a salicylate is treated with sodium nitrite and a little acetic acid, followed by a drop or two of copper sulphate solution, and the liquid boiled, a blood-red colour is produced, varying in intensity according to the amount of salicylic acid present. The test has been confirmed in Allen's laboratory and found very delicate. No similar reaction is produced by benzoic, cinnamic, or tartaric acid.

The most delicate reaction for salicylic acid and soluble salicylates is that with ferric salts, which produce a beautiful violet colour even in extremely dilute solutions. The reaction is much more delicate (1 in 100,000) than that of phenol with ferric salts (1 in 3,000). The violet colouration is destroyed by alkalis with precipitation of reddish-brown ferric hydroxide. It is also destroyed by mineral acids or others capable of liberating salicylic acid.[1] Certain neutral salts, such as phosphates, tartrates, citrates, and oxalates, also interfere more or less with the reaction.

Hence before applying the test it is necessary to isolate the salicylic acid from interfering substances such as are usually present in foods and beverages. For this purpose the sample is in most cases extracted with a solvent immiscible with water, the one generally recommended being the mixture of equal volumes of ether and light petroleum originally proposed by Taffe. Recently, however, Taffe has advocated the use of light petroleum alone (*Ann. Chim. anal.*, 1903, **8**, 84; *Bull. Soc. Chim.*, 1902, [iii], **27**, 701).

A definite volume of a beverage or, in the case of a solid food, the aqueous liquid obtained by boiling the sample with sodium hydroxide

[1] Weiske (*J. pr. Chem.*, 1875, [ii], **12**, 157) has proposed to employ the above reaction in alkalimetry. On neutralising an acid solution to which a trace of salicylic acid and ferric chloride have been added, the violet colour becomes gradually more developed until neutrality is reached, when the liquid turns reddish-yellow. But Pagliani (*Gazzetta*, 1879, **9**, 23) has shown that the amount of mineral acid required for the destruction of the violet colour varies greatly with the nature of the acid and the dilution of the liquid, and hence salicylic acid is ill-suited for use as an indicator. This is in accord with Allen's experience.

solution, is acidified with phosphoric acid and then shaken with the solvent. The extract is then shaken with dilute ferric chloride solution, when the production of a violet colouration in the aqueous layer indicates the presence of salicylic acid. The test becomes more delicate if the ethereal extract, instead of beng treated directly with the reagent, is shaken with dilute ammonia, the ammoniacal solution evaporated to dryness, the residue dissolved in the minimum quantity of water and the solution tested with ferric chloride.

For the extraction other solvents have been recommended. Thus Vitali (*Boll. chim. farm.*, 1906, **45,** 701) extracts wines with toluene. Although Gorni (*Rev. intern. Falsif.*, 1906, **19,** 16) has stated that tartaric acid is extracted from wines both by chloroform and by carbon disulphide, Dubois (*J. Amer. Chem. Soc.*, 1907, **29,** 293) advocates the use of the latter solvent as follows: The wine is extracted with ether and the ethereal solution evaporated to dryness. The residue is rubbed with 10 successive quantities (5 c.c. each) of carbon disulphide, the combined extracts evaporated, and the residue tested. The author states that carbon disulphide leaves undissolved several impurities which interfere with the colour reaction, chloroform redissolves some of the colouring matter extracted by the ether, whilst benzene, carbon tetrachloride, and light petroleum mixed with 10% of ether, dissolve salicylic acid with difficulty.

Ferreira da Silva (*Compt. rend.*, 1900, **131,** 423), Pereira (*Bull., Soc. Chim.*, 1901, [iii], **25,** 475), Mastbaum (*Chem. Zeit.*, 1903, **27,** 829), and Spica (*Gazzetta*, 1903, **33,** ii, 482) have shown that some, but not all, natural wines known to be free from added salicylic acid, give the colouration with ferric chloride characteristic of this substance. From the observations made by Pellet (*Ann. Chim. anal.*, 1901, **6,** 328), it seems to be established that the reaction is caused by traces of salicylic acid formed naturally. For this reason it must not be concluded that a sample of wine is adulterated if a minute trace of salicylic acid is detected in it. This source of error is avoided by the German official method in which not more than 50 c.c. of the wine are used for the test.

Some liquids are preferably subjected to a preliminary treatment before extracting with a solvent. Wine, beer, or urine may be treated with lead acetate, the filtrate precipitated with a slight excess of sulphuric acid and again filtered.

For the precipitation of casein from milk Pellet recommends the use of mercuric nitrate, but Revis and Payne state that this reagent

carries down a large proportion of the salicylic acid present. The method of coagulation advocated by Robin (*Ann. Chim. anal.*, 1909, **14**, 53) consists in slowly adding 50 c.c. of the milk to a mixture of 10 c.c. of 5% sulphuric acid and 20 c.c. of alcohol, and filtering until a clear filtrate is obtained. The latter is extracted as described above.

Experiments made by Ferreira da Silva (*Rev. intern. Falsif.*, 1901, **14**, 68) to determine the relative sensitiveness of various methods of extracting salicylic acid from wines, show that the most delicate is the original German official method (extraction of 50 c.c. with a mixture of ether and light petroleum) by which 1 part in 200,000 can be detected. The modified German process (extracting the residue from the ether-petroleum solution with benzene) shows 1 part in only 100,000 whilst the Weigert-Rosler method (extraction with carbon disulphide or chloroform) is equally sensitive.[1]

According to R. J. L. Schoepp (*Ned. Tydschr. Pharm.*, 1896, **7**, 67), the ferric chloride reaction is given by some specimens of beer undoubtedly free from salicylic acid, owing to the presence of *maltol*, a substance isolated by Brand from roasted malt. Sherman states (*J. Ind. Eng. Chem.*, 1910, **2**, 24) that a similar substance is present in baked cereal products and in roasted coffee. This substance, however, does not yield any characteristic reaction with Millon's reagent, with which salicylic acid gives a dark red colouration. Hence Schoepp considers it necessary in examining beer to use both tests.

In order to avoid the troublesome expedient of extracting the salicylic acid with an immiscible solvent, some authors have made use of the fact that the acid is volatile in steam. Thus Pellet (*Ann. Chim. anal.*, 1901, **6**, 364) boils 20 c.c. of the suspected liquid, acidified with phosphoric acid, and at intervals allows the escaping steam to condense on a glass rod. The liquid so condensed is added to a minute drop of ferric chloride solution, previously placed on a slightly greased porcelain plate. No reaction is obtained until the concentration of the salicylic acid in the boiling liquid has reached 0.06 to 0.07 grm. per litre, and therefore the method may be made roughly quantitative. A similar process, which is said to be particularly applicable to

[1] C. O. Curtman (*J. Pharm. Chim.*, 1886, [v], **14**, 523) recommends the formation of methyl salicylate for the detection of salicylic acid in wine or beer. He directs that 4 c.c. of the liquid to be tested should be mixed with 2 c.c. of methyl alcohol (or failing this, ordinary alcohol), and then 2 c.c. of pure sulphuric acid cautiously added. The liquid is agitated, heated for 2 minutes, allowed to cool for 10 minutes, and then heated just to boiling, when if salicylic acid were present, a distinct odour of wintergreen oil will be perceptible. With traces, it may be necessary to allow the liquid to cool again, and then heat a third time. In examining condensed milk, etc., by this process, the sample should be digested for some hours with dilute alcohol, and the filtered liquid concentrated and heated as above.

spirituous products, is described by von Genersich (*Zeitsch. Nahr. Genussm.*, 1908, **16**, 218–222).

Vitali (*Boll. chim. farm.*, 1906, **45**, 701) gives the following method for detecting salicylic acid in preserved tomatoes. The sample is acidified with hydrochloric acid, evaporated to a syrupy consistency, and extracted with absolute alcohol. The alcoholic extract is evaporated, the residue dissolved in a little water and the solution shaken with toluene. The toluene extract is tested for salicylic acid by shaking with dilute ferric chloride solution.

Instead of identifying the salicylic acid after extraction, by the colouration given with ferric chloride, Spica (*Gazzetta*, 1895, **25**, i, 207) has suggested the following test: The residue from the evaporation of the extract is heated with a few drops of nitric acid and excess of ammonia added. The small quantity of liquid obtained is heated with a thread of white wool, free from grease, which will be dyed bright yellow (by the picric acid formed) if salicylic acid were present. The author claims that 0.000001 grm. of salicylic acid can be recognised in this way. According to Montanari (*Gazzetta*, 1904, **34**, i, 290), the conversion into picric acid is complete only when sufficient nitric acid is used to allow the boiling to be continued for several minutes.

Estimation. Volumetric Methods.—In the absence of other substances of acid character, free salicylic acid can be accurately estimated by titration with alkali hydroxide. Phenolphthalein is the preferable indicator, but litmus may be used. 1 c.c. of decinormal alkali solution represents 0.0138 grm. of salicylic acid. Barium hydroxide solution is preferable to potash or soda for titrating salicylic acid, as its use ensures the absence of carbonate. It is not essential that the sample should be wholly in solution before commencing the titration, but toward the end of the process any salicylic acid still remaining undissolved should be brought into solution by warming the liquid. The above method of titration is available in presence of phenol.

Salicylic acid existing in the form of metallic salicylates can also be estimated by the foregoing titration method, provided the solution be first freely acidified with dilute sulphuric acid, and the liberated salicylic acid then extracted by agitation with ether or other solvent as already described. After separating, the immiscible solvent should be shaken twice with small quantities of water to remove traces of mineral acid. The dissolved salicylic acid may then be recovered

by cautious evaporation, but some loss by volatilisation is difficult to avoid. A preferable plan is to add a few drops of phenolphthalein solution, and titrate with standard baryta water, agitating between each addition. If desired, the immiscible solvent may then be separated from the neutral aqueous liquid, which may be evaporated, and the residual barium salicylate weighed or further examined.

The volatility of salicylic acid in a current of steam may be utilised for its separation from certain interfering substances, but the process is not to be recommended, as complete volatilisation is difficult to attain. The solution of the substance should be freely acidified with phosphoric acid and distilled to a low bulk, water being then added and the operation repeated several times, or until the fraction last obtained exhibits no acid reaction to phenolphthalein. Phenol, benzoic acid, and the 3 isomeric cresotic acids behave similarly to salicylic acid; but *m*- and *p*-hydroxybenzoic acids and hydroxyisophthalic acid are not volatile with steam. When the distillation process is to be applied to wine or beer, the liquid should be rendered alkaline with sodium hydroxide, reduced to half its bulk by boiling, to drive off the alcohol, and then acidified and distilled as described above. When only traces of salicylic acid are present, the distillate should be made alkaline and concentrated before acidifying and shaking with ether or applying other tests.

Freyer (*Chem. Zeit.*, 1896, **20**, 820) devised a method of estimating salicylic acid based on the determination of the amount of bromine which a given weight of the sample absorbs. Fresenius and Grünhut (*Zeitsch. anal. Chem.*, 1899, **38**, 292) and von Genersich (*loc. cit.*), after comparing the various methods suggested, have come to the conclusion that Freyer's process is the most accurate.

Salicylic acid is sometimes stated to be converted by treatment with bromine into dibromosalicylic acid, according to the reaction: $C_6H_4(OH).COOH + 2Br_2 = C_6H_2Br_2(OH).COOH + 2HBr$. It is probable that this equation correctly represents the action which first occurs, but numerous experiments by Allen and other observers prove that salicylic acid in aqueous solution ultimately reacts with 6 atoms of bromine ($3Br_2$), to form a *tri*brominated salicylic acid,[1]

[1] The constitution of this compound is uncertain. If it be $C_6H_2Br_2(OBr).COOH$, analogy with the substance $C_6H_2Br_3.OBr$ would lead one to expect that it would react with potassium iodide to form $C_6H_2Br_2(OH).COOH$, but this implies the combination of $2Br_2$ only, instead of $3Br_2$. On the other hand, the formation of the substance $C_6HBr_3(OH).COOH$ is not in accordance with the usual behaviour of ortho-derivatives of benzene, though it accounts for the absorption of $3Br_2$ (see E. Werner, *Bull. Soc. Chim.*, 1886, [ii], 46,, 275).

this subsequently splitting up into carbon dioxide and tribromophenol, according to the equation:

$$C_7H_3Br_3O_3 = CO_2 + C_6H_3Br_3O.[1]$$

Neither this change nor the conversion of the tribromophenol into the substance $C_6H_2Br_3OBr$ by the excess of bromine affects the process, since the former reacts with 6 atoms of bromine and the latter is converted into tribromophenol on treatment with potassium iodide in acid solution:

$$C_6H_2Br_3.OBr + 2HI = C_6H_2Br_3.OH + HBr + I_2.$$
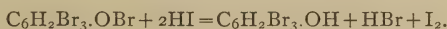
The process as carried out in Allen's laboratory is as follows: A known weight of the sample is dissolved in water (preferably with the aid of a little sodium hydroxide) and a volume corresponding to about 0.100 grm. of salicylic acid diluted to about 100 c.c. with water in a stoppered bottle. 10 c.c. of hydrochloric acid (sp. gr. 1.1) is next added (von Genersich states that it is preferable to add the salicylic acid solution to the bromate solution *after* the acidification of the latter), followed by a known volume (about 50 to 60 c.c.) of a solution containing sodium bromate and bromide, of which sufficient should be used to give about 75% of bromine in excess of that entering into the reaction.[2] The bottle is closely stoppered, well shaken, and allowed to remain in the dark for at least 1 hour to ensure the completion of the reaction.[3] Another bottle containing an equal quantity of the bromine solution is similarly diluted and acidified, and left to stand side by side with the sample. A solution of potassium iodide (10%) is next added to the contents of both bottles, and the liberated iodine titrated with a decinormal solution of sodium thiosulphate (24.827 grm. of $Na_2S_2O_3 + 5H_2O$ per litre). Each 1 c.c. of this thiosulphate solution required represents 0.008 grm. of bromine in excess of that which has reacted with the salicylic acid, 0.138 grm. of which causes the disappearance of 0.480 grm. of free bromine, or as much as will be liberated by about 50 c.c. of the bromine solution. The observation

[1] Allen has further proved that the change by which the 4 atoms of bromine at first absorbed is ultimately increased to 6 occurs gradually, the reaction being accompanied by an evolution of carbon dioxide, but even after many hours the volume of gas does not approach that represented by the above equation. Determinations of the percentage of bromine show that the product obtained is a mixture (Allen and Tankard).

[2] This solution is prepared by dissolving 19.5 grm. of bromine (=6.5 c.c.) in about 100 c.c. of water containing 10 grm. of sodium hydroxide. The liquid thus obtained is boiled well, and then diluted with water to 2 litres. The solution keeps indefinitely. On addition of hydrochloric acid, the whole of the bromine present is liberated according to the equation:
$$5NaBr + NaBrO_3 + 6HCl = 6NaCl + 3Br_2 + 3H_2O.$$
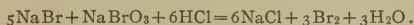
[3] A more prolonged standing is desirable when very accurate results are required.

of the end point may be assisted by the use of starch paste, but it is important that this should not be added until the liquid is nearly decolourised. Hence, if a preparation already containing starch is to be examined, the salicylic acid must first be extracted by alcohol or other suitable solvent, and the process applied to the solution (Fresenius and Grünhut). In the case of wine and beer, the salicylic acid should be first extracted by the use of a mixture of ether and light petroleum, and the process applied to the aqueous liquid obtained on shaking the above solution with sodium hydroxide.

The bromine process of estimating salicylic acid is specially valuable in presence of benzoic acid, which is not acted on by bromine in aqueous solution. The precipitate may be filtered off, and the benzoic acid isolated from the filtrate. Cinnamic acid reacts with 4 atoms of bromine.

Telle (*J. Pharm. Chim.*, 1901, [vi], **13,** 49) has proposed a somewhat similar method. This depends on the observation that when sodium hypochlorite solution is added to a solution of potassium bromide acidified with hydrochloric acid and containing salicylic acid, no bromine is liberated until the latter is completely converted into dibromosalicylic acid.

Messinger and Vortmann (*Ber.*, 1890, **23,** 2753) propose to precipitate salicylic acid from its alkaline solutions, by iodine, as sodium di-iodosalicylic iodide, afterwards titrating the excess of iodine with sodium thiosulphate. The reaction takes place as follows:

$$C_6H_4(OH).COONa + 3NaOH + 3I_2 = C_6H_2I_2(OI)COONa + 3NaI + 3H_2O.$$
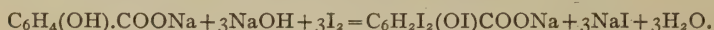
W. Fresenius and Grünhut (*Zeit. anal. Chem.*, 1899, **38,** 292) have criticised the method adversely, but Messinger has shown that, under proper conditions, it gives accurate results (*J. pr. Chem.*, 1900, [ii], **61,** 236).[1] The process is also applicable to the estimation of phenol, thymol, and β-naphthol. The methods of Freyer and of Messinger and Vortmann are unfavourably criticised by Seidell (*J. Amer. Chem. Soc.*, 1909, **31,** 1168) who advocates the following as more satisfactory.

[1] F. B. Power considers the process fairly accurate. Too large an excess of alkali should not be used. He gives the following data for one of his experiments: 0.4782 grm. of bismuth salicylate was dissolved in hydrochloric acid, the bismuth precipitated by sodium hydroxide, the liquid filtered, and the filtrate made up to 250 c.c. 50 c.c. of this solution were neutralised in a stoppered bottle with sulphuric acid, and then 0.5 c.c. of a 10% solution of sodium hydroxide added. The bottle was immersed in hot water, and when the contents were at 60°, 31 c.c. of decinormal iodine solution were added, and the flask kept warm and occasionally shaken for a few minutes. The liquid was then cooled, acidified with sulphuric acid, filtered, and the precipitate washed with a little water. The filtrate required 15.1 c.c. of thiosulphate, showing that the iodine of 15.9 c.c. had been absorbed. As 1 c.c. of decinormal iodine corresponds to 0.0023 grm. of salicylic acid, this indicated 38.25% in the bismuth salt, against a calculated amount of 38.45%.

A known weight of the sample of salicylate dissolved in a small quantity of water is introduced into a stoppered bottle and treated with 50 c.c. of strong hydrochloric acid. The solution is titrated with $N/5$ bromate solution, the liquid being shaken and warmed gently after each addition. The bromate solution is added until the yellow colour of free bromine persists for 5 minutes after the addition of the last two drops, the liquid having a temperature of 80° to 100°. In this reaction one molecule of salicylic acid absorbs two molecules of bromine. A variation in the method consists of treating the salicylic solution with excess of bromate, and estimating the unabsorbed bromine with standard stannous chloride solution.

Gravimetric Method.—According to Bougault (*Compt. rend.*, 1908, **146**, 1403), the substance obtained by Messinger and Vortmann by the action of iodine on salicylic acid is a mixture of potassium 3:5-di-iodosalicylate with the red substance described by Lautemann (*Annalen*, 1861, **120**, 309) which was shown by Benzinger and Kammerer (*Ber.*, 1878, **11**, 557) to be tetraiododiphenylenequinone. The extreme insolubility of the latter substance furnishes a method of estimating salicylic acid, which is especially applicable in the presence of cinnamic acid. A weight of the sample containing approximately 0.1 grm. of salicylic acid is dissolved in a solution of 1 grm. of sodium carbonate in 50 c.c. of water. Excess of iodine is added, the liquid heated for 20 minutes on a water-bath, and then boiled for 10 minutes under a reflux condenser, iodine being added from time to time to ensure the presence of excess. After removing the excess of iodine with sodium sulphite, the precipitate is collected on a Gooch crucible, washed, dried, and weighed. The weight multiplied by $138/344$ gives the weight of salicylic acid. *p*-Hydroxybenzoic acid reacts with iodine, giving the same substance.

For the estimation of salicylic acid in wine, Bigelow treats 100 c.c. of the sample with 5 c.c. of sulphuric acid (1:3) and extracts with 50 c.c. of carbon tetrachloride or toluene. 25 c.c. of the extract are evaporated in a tared flask and the residue weighed. The latter may afterwards be dissolved in alcohol and the solution titrated with $N/100$ baryta. If the proportion of acid present is less than 0.025 grm. per 100 c.c. it is more accurately estimated colourimetrically. (*U. S. Dept. Agric. Bull.*, No. 122, 1909, 64.)

Colourimetric Methods.—The ferric chloride reaction may be employed for the approximate colourimetric estimation of salicylic acid.

When the operation is performed on the original liquid, instead of using an aqueous solution of salicylic acid as the standard of comparison, it is preferable in all cases to add a definite amount of salicylic acid to a liquid of the same kind as that in which the salicylic acid is to be estimated. Thus milk should be compared with milk, beer with beer, and urine with urine, and the standard specimen submitted to the same treatment as the sample to be compared with it. But in all cases it is preferable to extract the salicylic acid with ether before applying the iron test, as many substances weaken the colour-reaction or suppress it entirely. The ferric chloride solution should be very dilute, and must be added gradually till the colouration no longer increases. With small quantities of salicylic acid an excess of ferric chloride destroys the colouration.[1]

The following method of applying the ferric chloride reaction to the estimation of salicylic acid in organic liquids and in foods, described by S. Harvey (*Analyst*, 1903, **28**, 2), has given good results in Allen's laboratory.[2] Standard solutions of pure salicylic acid are prepared, containing, respectively, 0.100 and 0.010 grm. of the acid per 100 c.c. The salicylic acid is suspended in water and dissolved by adding a slight excess of sodium hydroxide solution, and the liquid then rendered neutral to phenolphthalein by decinormal sulphuric acid. The solutions should be freshly made when required. The use of hydrochloric acid throughout the process should be avoided, as it seems to interfere with the colouration. A 1% solution of iron-alum is used to produce the violet colouration, which is purer and more stable than that obtained with ferric chloride. The alum solution should be acidified with a few drops of dilute sulphuric acid per 100 c.c.

The liquid under examination is acidified with sulphuric acid, and extracted with a mixture of light petroleum and ether as already described. Syrupy and strongly alcoholic liquids should be somewhat diluted before extraction with the mixed solvents. 2 successive shak-

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[1] According to Fajans (*Chem. Zeit.*, 1893, **17**, 69), the colourimetric estimation of salicylic acid by means of ferric chloride cannot be carried out in the presence of phenols. Advantage may be taken, however, of the fact that the latter give no colour with a solution of ferric chloride in absolute alcohol. To estimate salicylic acid, the suspected liquid is acidified and extracted with ether, the solvent being allowed to evaporate spontaneously. The residue is dissolved in 25 to 30 c.c. of absolute alcohol, introduced into a graduated tube, and mixed with a few drops of a 5% solution of ferric chloride in absolute alcohol, until the colour ceases to darken. In a similar tube the same amount of an alcoholic solution of salicylic acid (2 in 10,000) is taken, and then a sufficiency of ferric chloride solution. Finally the darker of the two mixtures is diluted with absolute alcohol until they both show the same intensity of colour; the difference in volume is noted, and the amount of salicylic acid thus found. According to Fajans, by this process 1 part of salicylic acid in the presence of 800 parts of phenol may be accurately estimated.
[2] Pellet and de Grobert (*Bull. Assoc. chim. sucr. dist.*, 1902, **20**, 289) have described a similar method.

ings with the solvent are sufficient, and but little colouring matter is dissolved. The separated solvent is next shaken with 2 successive quantities of water containing a known amount (5 c.c.) of decinormal alkali hydroxide, the aqueous liquid being separated, carefully neutralised, and diluted to 250 c.c. or 500 c.c.[1] A known volume of this liquid is withdrawn, diluted if necessary to 100 c.c., and 1 or 2 c.c. of the iron-alum solution added. The operation is conveniently carried out in Nessler glasses, a standard being obtained in the same way by using the weaker of the 2 solutions of salicylic acid described above. The maximum amount of salicylic acid capable of being compared by this colourimetric process is 0.001 grm. per 100 c.c., but less than this amount is preferable.

For the estimation of salicylic acid in foods and beverages containing tannin, Harry and Mummery have devised a process (*Analyst*, 1905, **30**, 124) based on the fact that lead tannate is insoluble in alkalis, whilst lead salicylate is readily soluble. In the case of jam, fruit pulp, or similar substances, 50 grm. of the crushed sample are introduced into a 300 c.c. flask together with a little water and 15 to 20 c.c. of a saturated solution of basic lead acetate. The mixture is made alkaline by the addition of 25 c.c. of approximately normal sodium hydroxide solution, and after well shaking, 15 to 20 c.c. of N-hydrochloric acid are added and the whole diluted to 300 c.c. The partial neutralisation of the alkali is required in order to obtain complete solution of the lead salicylate. After well mixing, the contents of the flask are filtered, 200 c.c. of the filtrate are acidified with hydrochloric acid, again filtered if necessary, and extracted 3 times with ether. The residue left after evaporating the combined ethereal extracts is dissolved in alcohol, the solution diluted to 100 c.c. and the salicylic acid estimated colourimetrically with ferric chloride. These authors disagree with Harvey as to the advisability of using iron-alum solution, particularly in the acid condition.

In the case of milk and cream, Revis and Payne have obtained satisfactory results by the following process (*Analyst*, 1907, **32**, 286): 20 c.c. of the milk or 20 grm. of the cream are introduced into a stoppered flask and rendered exactly neutral to litmus by adding N-sodium hydroxide solution, the volume added being noted. 40 c.c. of

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[1] The use of distilled water throughout the process is imperative. The accuracy of the method is impaired by the presence of more than small amounts of saline matter in the solution to be compared, and the slightest alkalinity is fatal to success. The slight acidity due to the iron-alum solution is an advantage.

neutral absolute alcohol are added, the flask stoppered securely, and immersed in water at 95° for 15 minutes with frequent shaking (this is essential). After cooling a volume of water equivalent to that of the proteins and fat less that of the alkali solution used for neutralisation, is added. For milks this correction may be taken as 2 c.c., but for creams it depends on the percentage of fat. To 20 grm. of cream containing 55% of fat 12.5 c.c. of water must be added, with 50% of fat 11.4 c.c., 40% of fat 9.3 c.c., 30% of fat 7.2 c.c., and so on. The mixture is then filtered or, better, separated by means of a centrifugal machine. 40 c.c. of the clear filtrate are introduced into a flask with 100 c.c. of water and sufficient sodium hydroxide to make the liquid distinctly alkaline, and distilled until 60 c.c. of distillate have been collected. The residue is transferred to a 250 c.c. measuring flask, treated with 2 c.c. of a potassium mercuric iodide solution, prepared by dissolving 1.35 grm. of mercuric chloride and 3.32 grm. of potassium iodide in 64 c.c. of water and adding 20 c.c. of concentrated sulphuric acid, and diluted to 250 c.c. (in the case of cream a further 1 c.c. of water is added to allow for the slight precipitation of protein). After standing for a few minutes the liquid is filtered and 100 c.c. of the filtrate extracted 3 times with ether, using 20 c.c. at each extraction. The combined ethereal extracts, after washing with a little water, are mixed with 20 c.c. of water and 1 drop of phenolphthalein solution, and $N/10$ sodium hydroxide solution added until, on shaking, the lower (aqueous layer) remains red. 1 c.c. excess of the alkali is added and, after well shaking, the aqueous layer is separated. The ether is again extracted with 20 c.c. of water containing 1 c.c. of $N/10$ alkali, and finally with 20 c.c. of water. To the combined aqueous extracts, $N/10$ sulphuric acid equivalent to the alkali used, is added, the solution diluted to 100 c.c. and examined colourimetrically in the usual manner. A concentration of salicylic acid of 0.001–0.002% (not more) gives the most suitable colouration. The iron solution is best prepared by diluting a 1% ferric alum solution with 5 volumes of water and then evaporating to the original bulk. The reagent thus treated does not precipitate the test solution. Boric and benzoic acids do not interfere in this method.

Dubois (*J. Amer. Chem. Soc.*, 1906, **28**, 1616) states that salicylic acid cannot be successfully separated from tinned tomatoes either by extraction with light petroleum or by steam distillation. He recommends the following procedure: 50 grm. of the pulped sample are in-

troduced into a 200 c.c. flask with 50 c.c. of water, the mixture neutralised with ammonia, and 15 c.c. of milk of lime (1:10) added. The product is diluted to 200 c.c., well shaken, and filtered. 150 c.c. of the filtrate are extracted 4 times with 25 c.c. (each time) of ether, and the combined ethereal extracts washed twice with water. The ethereal solution is distilled until only 20 to 25 c.c. remain, and the residue is allowed to evaporate spontaneously. The solid residue is dissolved in hot water and the salicylic acid estimated colourimetrically.

METALLIC AND ALKALOIDAL SALICYLATES.

Sodium salicylate, $NaC_7H_5O_3$, H_2O forms small white crystalline plates or a crystalline powder, odourless and permanent in the air. It has a sweetish, saline and somewhat alkaline taste, and a neutral or feebly acid reaction to litmus. It is soluble in an equal weight of cold water, only slightly soluble in absolute alcohol, but soluble in 8 parts of cold rectified spirit. In boiling water and alcohol sodium salicylate is very soluble. Both the alcoholic and the aqueous solutions give a violet colour with ferric chloride. On ignition, sodium salicylate evolves phenol, and leaves from 30 to 31% of Na_2CO_3. It is completely soluble in ammonia, and the solution does not reduce silver nitrate, even on boiling. Barium chloride should cause no precipitate in the aqueous solution, and the precipitate with silver nitrate should completely dissolve on addition of nitric acid and alcohol. When the solid salt is shaken in the cold with 15 parts of strong sulphuric acid, no brown colouration should be produced.

The British Pharmacopœia (1898) states that solutions of sodium salicylate, not more dilute than 1% strength, give a yellowish-brown precipitate with uranium nitrate solution (distinction from carbolates and sulphocarbolates). With only a small quantity of the uranium nitrate solution, the liquid is coloured brown, but no precipitation occurs. Larger quantities of the reagent give the yellow-brown flocculent precipitate of *uranyl salicylate,* which subsequently acquires a "silky" appearance.

As in the case of salicylic acid, 3 qualities of sodium salicylate are recognised in commerce. Especially if not quite pure, sodium salicylate is liable to become coloured by keeping. This change is more marked when the salt is exposed to air and light. The same is true

of the solution, but this may be preserved by the addition of about 1% of sodium thiosulphate.

For the assay of sodium salicylate Alcock (*Pharm. J.*, 1906, [iv], **23,** 597) advocates the following method: 0.5 grm. of the sample and 0.5 grm. of ammonium chloride are dissolved in 10 c.c. of water, and the solution evaporated to dryness in a platinum dish. Salicylic acid, ammonia and phenol (if present) are evolved during this evaporation. The residue is gently ignited, cooled, and the residual sodium chloride dissolved in water and the solution titrated with $N/10$ silver nitrate solution, of which 31.2 c.c. should be required. A preliminary estimation must be made of the chloride present in the sample.

Lithium salicylate, $LiC_7H_5O_3$, forms a white crystalline powder, readily soluble in water and alcohol. As met with in commerce, it usually has an acid reaction. The solubility of this salt in water at 15° is about 1:0.8, and in alcohol about 1:1.7. Lithium salicylate is employed (in doses of 0.5 to 1.0 grm.) in the treatment of acute or chronic rheumatism.

Ferric salicylate, $Fe(C_7H_5O_3)_3$, separates, on mixing a strong solution of sodium salicylate with ferric chloride, as a brown precipitate, which, together with the mother liquor, rapidly acquires a deep violet colour. After washing, ferric salicylate forms a brown amorphous substance, which yields a violet solution on boiling with water.

Strontium salicylate, $Sr(C_7H_5O_3)_2$, forms sparingly soluble crystals. It is highly recommended as an internal antiseptic in place of salol, and in chronic gout and rheumatism, especially when complicated by nervous disorders.

Aluminium salicylate, $Al_2(C_7H_5O_3)_6 + 3H_2O$, is obtained as a precipitate on mixing solutions of an aluminium salt and sodium salicylate. It occurs in commerce under the name of "*Salumen*" as a reddish-white, insoluble powder, which is employed as a dusting powder in catarrhal affections of the nose and pharynx.

Aluminium ammonium salicylate, $Al_2[C_6H_4(ONH_4)CO_2]_6 + 2H_2O$, is a neutral soluble salt which is more stable in solution than in the dry state. Under the name of "*Soluble Salumen*" it is used as an astringent wash for the throat and nasal passages.

Aluminium potassium salicylate has been employed as a combined astringent and antiseptic under the name "*Alkasal*" or "*Alkasol*." Alkasal is also the name given to an aluminium potassium acetate.

Mercuric Salicylate. —A basic compound of the formula $C_6H_4 \langle {}^{CO_2}_O \rangle Hg$ is obtained by mixing solutions of mercuric nitrate and sodium salicylate, and is now official in the German Pharmacopœia (Edit. iv). It forms a white amorphous powder, insoluble in water and chloroform, but soluble in a solution of sodium chloride and other haloid salts. Freshly-prepared mercuric salicylate is more soluble, and gives a stronger ferric chloride reaction than old samples. Mercuric salicylate is also somewhat soluble in ether (1:100) and in 95% alcohol (1:45). After keeping for some time, the salt has an acid reaction to litmus. Mercuric salicylate keeps best in solution in sodium chloride. Mercuric salicylate is decomposed by a solution of sodium carbonate.

E. Rupp (*Arch. Pharm.*, 1901, **239,** 114) states that the method given in the German Pharmacopœia for the estimation of the mercury in mercuric salicylate (precipitation of mercuric sulphide by hydrogen sulphide) is unreliable, and recommends that 0.3 grm. of the salicylate should be rubbed down with a little water and 25 c.c. of decinormal iodine solution run in. After standing for an hour in a well-stoppered flask, the excess of iodine is determined by titration with standard thiosulphate solution. Several estimations required 16.5 to 16.8 c.c. of decinormal iodine, practically no variation being noticed whether the action was allowed to continue for 1 hour or 15. Theoretically, 0.3 grm. of the salicylate should require 17.85 c.c. of decinormal iodine solution. The low results obtained are due to the fact that mercuric salicylate reacts with haloid salts to form a double compound, but as this is a constant, the results are quite reliable.

Bismuth salicylate, or, more correctly, *Bismuthyl Salicylate* $BiO . C_7H_5O_3 + H_2O$,[1] is employed to a considerable extent in medicine. It is a white amorphous powder, insoluble in water. The British Pharmacopœia (1898) requires that when the substance is shaken with alcohol of 90%, the filtered liquid shall give no colour with ferric chloride (indicative of free salicylic acid). It is further required that, when precipitated with hydrogen sulphide, the salt should yield 70% (the theoretical quantity is 71%) of bismuth sulphide, Bi_2S_3.

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[1] According to Martinotti and Cornelio (*Boll. Chim. farm.*, 1901, **40,** 141), commercial bismuth salicylate contains one or both of the following compounds:
$C_6H_4(OH) . COOBiO$; and $C_6H_4(OH) . COOBi(OH)_2$.
P. Thibault, however (*J. Pharm. Chim.*, 1901, [vi], **14,** 22; *Bull. Soc. Chim.*, 1901, [iii], **25,** 794), has obtained a true bismuth salicylate, having the formula $Bi_2O_3 . (C_7H_6O_3)_3$.

The theoretical quantity of Bi_2O_3 which should be obtained on heating and cautious ignition of bismuth salicylate is 64.3%, but the salt is very liable to yield slightly more oxide. The British Pharmacopœia of 1898 requires from 62 to 64% of bismuth oxide.[1]

The use of alcohol as a solvent for free salicylic acid in bismuth salicylate is unsatisfactory, since it causes partial decomposition of the latter. W. Lyon (*Pharm. J.*, 1904, [iv], **18,** 219) prefers to employ 90% benzol, which is free from this objection.

Harrison (*Pharm. J.*, 1908, [iv], **27,** 349) recommends the use of ether for the same purpose.

In the examination of bismuth salicylate the determination of the proportion of bismuth oxide left on ignition will usually be found a sufficient indication of quality, but the salicylic acid may also be separated by acidifying the solution with hydrochloric acid and agitating with ether, when the residue, left on evaporation of the ether, may be examined for *p*-cresotic acid.

Although commercial samples of bismuth salicylate may easily be obtained of a fair standard of purity, the percentage of Bi_2O_3 is very variable. From 30 to 75% of the oxide have been found by various observers.

D. B. Dott (*Pharm. J.*, 1895, [iv], **1,** 582) has described a sample of so-called bismuth salicylate which contained 47% of free salicylic acid, as etimated by treatment of the sample with ether. Bismuth salicylate is extensively employed for the treatment of gastric catarrh and some intestinal disorders, but the presence of more than insignificant traces of free acid renders the preparation objectionable. Samples having an exceptionally light colour generally contain a notable quantity of free acid.

Commercial bismuth salicylate is very liable to contain small quantities of bismuth *nitrate*, and, according to Green and Windridge (*Pharm. J.*, 1900, [iv], **10,** 262), this impurity is always present. For its detection, they dissolve the sample in pure sulphuric acid and add the liquid to a solution of brucine in the same acid. This latter often has a pink or rose colour, but in the presence of traces of nitrates the

[1] It has been pointed out by several observers that no sample of bismuth salicylate, however carefully prepared, will answer to the official requirements, as the portion extracted by alcohol will invariably give a violet reaction with ferric chloride, whilst the percentage of bismuth oxide will often reach as much as 66 even in the most carefully prepared specimens. F. B. Power points out that the pharmacopœial requirements are inconsistent, since if less than 64.3% of bismuth oxide is present there must necessarily be a corresponding excess of salicylic acid, which will give a violet colouration with ferric chloride when shaken out with alcohol.

colour becomes a bright red which cannot be mistaken. The reaction with indigo has also been proposed for the detection of nitrate in bismuth salicylate.

I. Kollo (*Proc. Amer. Pharm. Assoc.*, 1899, p. 719) has proposed to assay bismuth salicylate by heating a known weight with excess of normal sodium hydroxide, filtering off and weighing the resultant $BiO.OH$ (or igniting it to Bi_2O_3), and calculating the salicylic acid from the diminished alkalinity of the filtrate. The results are not very accurate, and any nitrate of bismuth present in the sample will be calculated as salicylate.

F. B. Power has found that Messinger and Vortmann's iodine process (page 482) can be satisfactorily employed for the assay of bismuth salicylate.

Bismuth cerium salicylate forms an insoluble pink powder which has proved valuable in the treatment of diseases of the gastric and intestinal mucous membranes.

Sodio-theobromine Salicylate.—A compound of the formula $C_7H_7N_4O_2Na + C_6H_4(OH).COONa$, has received application in medicine under the name of "Diuretin." It is prepared by mixing aqueous solutions of molecular proportions of sodium salicylate and sodium-theobromine, and evaporating to dryness.

According to Sztankay (*Pharm. Post.*, 1898, **31**, 189), diuretin has the composition $C_7H_8N_4O_2NaOH.OH.C_6H_4.CO_2Na$, whilst the true sodio-theobromine salicylate, $C_7H_8N_4O_2.OH.C_6H_4CO_2Na$, can be prepared by adding theobromine to warm sodium salicylate solution as long as it dissolves and then allowing to crystallise. It is less soluble in water than diuretin (*Pharm. Zeit.*, 1899, **40**, 29).

Diuretin is a white amorphous powder, freely soluble in water, but decomposed by acids. It is employed as a diuretic in cases of scarlet fever, nephritis, etc. (dose: adults, 20 to 40 grains; children, 8 to 24 grains). "*Uropherin*" is the lithium compound corresponding to diuretin. It is recommended as a diuretic in doses of 15 grains.

Antipyrine salicylate is known commercially as "*Salipyrin.*" It is an odourless crystalline powder melting at about 91°. It has a pleasant taste, and possesses the properties of its constituents.

Altschul states (*Pharm. Centr. Halle*, 1893, **33**, 61) that phenolphthalein is not coloured by antipyrine and that consequently the salicylic acid in a sample of salipyrin can be titrated with standard alkali.

Tolypyrine salicylate, commercially known as *"Tolysal,"* melts at 101°, and closely resembles salipyrin.

Quinine salicylate is used to a considerable extent as an antipyretic in typhus, and as a remedy for gout and rheumatism. It forms fine white needles of the formula $C_{20}H_{24}N_2O_2,C_7H_6O_3+H_2O$. It should contain 70% of quinine, but is very liable to be contaminated with excess of salicylic acid, for which impurity it should always be examined. Quinine salicylate dissolves in about 225 parts of cold water, in 20 parts of 90% alcohol, and in 25 parts of chloroform.

"Saloquinine," $C_6H_4(OH).COO.C_{20}H_{23}N_2O$, the quinine-ester of salicylic acid, has been recommended as an analgesic; and *"Rheumatine,"* the salicylate of saloquinine, is said to be of value in rheumatic affections.

Colchicine salicylate, known in commerce as *"Colchisal,"* is used, in doses of 1/100 of a grain, in the treatment of arthritis, gout, and rheumatism. It forms a yellow amorphous powder, soluble in water, alcohol, and ether. The name "colchisal" is also applied to a mixture of colchicine and methyl salicylate. The preparation is dangerous in cases of kidney disease.

SALICYLIC ESTERS.

Several of the esters of salicylic acid are of considerable commercial importance, and this is specially the case with the methyl and phenyl esters.

Methyl Salicylate, $C_6H_4(OH).COO(CH_3)$.—This compound occurs naturally in the leaves of the *Wintergreen (Gaultheria procumbens)* and the bark of the *Sweet Birch (Betula lenta)*, and the essential oils from these sources consist of methyl salicylate in an approximately pure condition. Methyl salicylate occurs in smaller proportion in various other plants,[1] but usually in the form of the crystallisable glucoside *gaultherin,* which under the influence of the soluble ferment *betulase* splits up into dextrose and methyl salicylate: $C_{14}H_{18}O_8 + H_2O = C_6H_{12}O_6 + C_6H_4(OH).COO(CH_3)$. The ester of wintergreen leaves and betula bark exists chiefly in the form of the glucoside, but in the former case some ready-formed methyl salicylate is also present.

In addition to the foregoing natural sources, methyl salicylate is now manufactured synthetically on a considerable scale, by distilling 2 parts of salicylic acid with 2 of methyl alcohol and 1 of strong sul-

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[1] The salicylic acid detected in certain fruits is probably present as methyl salicylate.

phuric acid. An alternative process, which is said to give good results, is to pass dry hydrochloric acid gas through a saturated solution of salicylic acid in methyl alcohol (H. T. Thayer, *Amer. Jour. Pharm.*, 1895, **67**, 243; *Pharm. J.*, 1895, [iii], **25**, 1090).

Pure methyl salicylate is a colourless or yellowish oil of peculiar aromatic odour. It has a sp. gr. of 1.1819 at 16°, and boils under the ordinary atmospheric pressure at 224°. If shaken with water and the aqueous liquid then treated with ferric chloride a deep violet colouration is produced. When boiled with sodium hydroxide methyl salicylate is hydrolysed with the formation of methyl alcohol and a salicylate, but with cold, dilute potassium hydroxide solution it reacts to form a crystalline compound of the formula $C_6H_4(OK).COOMe$.

Methyl salicylate is now manufactured in a state of considerable purity, and is extensively used in the treatment of rheumatism and kindred affections. It is known in commerce as "artificial wintergreen or gaultheria oil," and is said to be preferable to the natural oils of wintergreen and sweet birch, as being less liable to adulteration.[1]

Estimation.—Gibbs (*J. Amer. Chem. Soc.*, 1908, **30**, 1465) describes the following method for estimating methyl salicylate in foods and drugs: The substance is extracted with *N*-sodium hydrogen carbonate solution, which dissolves the salicylic acid and a part of the ester. The remainder of the latter is isolated by acidifying with dilute sulphuric acid and distilling in steam. Both the distillate and the alkaline solution are extracted with chloroform, the chloroform extracts are boiled in a reflux apparatus with excess of potassium hydroxide and the salicylic acid liberated is estimated.

Natural gaultheria or wintergreen oil (from *Gaultheria procumbens*) contains about 99% of methyl salicylate (Power and Kleber[2] *Pharm. Rundschau*, 1895, **13**, 228). The remaining 1% was isolated by repeatedly shaking an ethereal solution of the oil with potassium hydroxide solution, as described under birch oil (page 494). Only 1.05% of the sample survived this treatment, and on evaporation of the ether was obtained as a mass which was semi-solid at the ordinary temperature. Power and Kleber isolated from it the following substances: A *paraffin*

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[1] In large quantities, methyl salicylate has marked toxic properties. A fatal case of poisoning of a middle-aged farmer who took two ounces of wintergreen oil in mistake for whisky has been recorded by B. Pillsbury (*New York Med. Record*, **58**, 150). Death occurred from exhaustion in 41 hours.

[2] Cahours, in 1844, found wintergreen oil to contain 90% of methyl salicylate and 10% of a terpene boiling at 160°, which he called "gaultherilene." Recent analyses of gaultheria oil have failed to confirm this observation and it is highly probable that the oil examined by Cahours was adulterated with turpentine oil.

m. p. 65.5° and of the probable formula $C_{30}H_{62}$; an *aldehyde* or *ketone*, which when separated in a pure form from its hydrogen sulphite compound had an odour like that of œnanthic aldehyde; a secondary *alcohol*, $C_8H_{16}O$, b. p. 160° to 165° corresponding to the above aldehyde or ketone; and an *ester* which on saponification yielded the above alcohol and an acid containing $C_6H_{10}O_2$, resulting by oxidation from the ketone.[1] The alcohol and ester possessed the penetrating characteristic odour which distinguishes wintergreen oil from artificial methyl salicylate, and gives the natural product its special value as a perfume.

True gaultheria oil is a colourless, yellow, or reddish liquid of a characteristic, strongly aromatic odour, which is different from that of birch oil or artificial methyl salicylate. The sp. gr. of the natural oil ranges from 1.180 to 1.187, and the b. p. from 218° to 221°. The oil is readily soluble in alcohol, ether, chloroform, and glacial acetic acid.

True gaultheria oil (now commercially almost obsolete) differs from birch oil and artificial methyl salicylate in being feebly optically active, the value of $[a]_D$ being —0.25° to —1°. This character is the only one besides the odour by which gaultheria oil is distinguishable from sweet birch oil, which is now very generally substituted for it.

Oil of sweet birch is prepared from the bark of *Betula lenta*, a tree growing extensively in some of the older of the United States.[2] It is colourless or yellowish, but sometimes has a reddish tint from the presence of traces of iron. In odour and taste birch oil is practically indistinguishable from pure methyl salicylate, in both of which respects it differs from wintergreen oil. The optical neutrality of birch oil also distinguishes it from wintergreen oil, but the sp. gr. and b. p. are identical for the two oils.

According to Power and Kleber (*loc. cit.*), sweet birch oil is composed almost wholly of methyl salicylate, of which it contains 99.8%. To separate the small proportion of other constituents, Power and Kleber dissolve the oil in ether, and shake with a 7.5% solution of potassium hydroxide in water, when potassium methyl salicylate passes into the aqueous liquid and the other constituents are retained by the ether. By evaporation of the separated ether Power and Kleber obtained a residue from which they isolated a paraffin and ester apparently iden-

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[1] Trimble and Schröter found wintergreen and birch oils to contain traces of alcohol and benzoic acid.

[2] On the Production and Purification of Oil of Birch see the *Scientific American*, June 13, 1801: *Amer. Journ. Pharm.*, Dec., 1891; *Pharm. J.*, 1892, [iii], **22**, 593.

tical with those found by them in gaultheria oil; but the secondary alcohol accompanying these compounds was not found in birch oil. Both the natural and artificial varieties of methyl salicylate resemble salicylic acid in giving a deep violet colouration when their alcoholic or aqueous solutions are treated with ferric chloride.

The commercial forms of methyl salicylate, especially those of so-called natural origin, are liable to adulteration with alcohol, chloroform, sassafras oil, oil of camphor, and petroleum. The sp. gr. of the sample affords a good indication of sophistication, since all the above-named adulterants except chloroform are of less density than methyl salicylate. The solubility of the oil in 70% alcohol is also decreased by the presence of most adulterants.

If either of the forms of methyl salicylate be treated in a graduated tube with 10 volumes of a 5% aqueous solution of potassium hydroxide, it dissolves entirely, either at once or on placing the tube in boiling water, whereas any admixed oils remain undissolved, and if present in sufficient proportion can be measured. As the odour of the methyl salicylate is entirely destroyed by the treatment with alkali, the presence of chloroform and other adulterants of strong odour becomes apparent at this stage. The residual odour also distinguishes true gaultheria oil from oil of sweet birch or artificial methyl salicylate.

Chloroform may also be detected by the smell when the oil is warmed. Samples containing chloroform have a high density and low b. p., whilst the density is diminished by the presence of *alcohol*. The chloroform may be approximately separated and estimated by fractional distillation, or by estimating the hydrochloric acid formed on passing the vapour mixed with hydrogen through a red-hot tube. In the portion from which the alcohol and chloroform have been separated by distillation, oil of sassafras may be recognised by its odour after addition of a hot concentrated solution of potassium hydroxide. *Sassafras oil* may also be detected by adding 3 or 4 drops of nitric acid (sp. gr. 1.3 to 1.4) to 4 or 5 drops of the oil. Sassafras oil becomes blood-red in colour, and soon changes to a brown or dark red amorphous mass. Pure methyl salicylate is unchanged at first, but after some hours it solidifies to a mass of colourless crystals, consisting of methyl nitrosalicylate.

The presence of *petroleum* greatly modifies the solubility of methyl salicylate in alcohol, besides reducing the sp. gr. *Oil of camphor* will be rectified before being used as an adulterant. If the lighter frac-

tions be employed, these will reduce the sp. gr. of the sample and render it optically active; and the terpenes of the camphor oil can be distilled off and further examined. The heavier fractions of camphor oil contain much safrole, which can be recognised by its odour after the methyl salicylate has been saponified.

A useful control on the foregoing tests is obtained by actual estimation of the real methyl salicylate present. This may be effected by saponifying the oil with a known quantity of potassium hydroxide, and determining the excess by titration with standard acid and phenolphthalein, as in Koettstorfer's method for oils; by acidifying the liquid after saponification, extracting the liberated salicylic acid with ether, and titrating the separated ethereal solution; or by treating the sample with alkali and standard iodine, and titrating the acidified liquid with standard thiosulphate, as practised by Messinger and Vortmann. Although the oils from *Gaultheria procumbens* and *Betula lenta* contain other esters which are expressed in terms of methyl salicylate when the saponification method of assay is employed, Schimmel & Co. prefer that process to the iodine method.

Schneegans and Gerock (*Pharm. Centralb.*, 1892, **33**, 40) recommend the following as a satisfactory method of detecting free salicylic acid in such substances as artificial oil of wintergreen. One volume of the oil is shaken with 500 volumes of water, and to 100 c.c. of the liquid is added 1 c.c. of a very dilute solution of ferric chloride. If, on the addition of 5 c.c. of chloroform, the violet colour formed disappears, free salicylic acid is absent; but if it persists, the acid is present. This reaction is said to be reliable to the extent of 0.02 mg. in 1 grm. of the oil.

Gibbs (*loc. cit.*) estimates free salicylic acid in oil of gaultheria by shaking 5 to 20 c.c. with water and titrating the aqueous solution with $N/50$ sodium hydrogen carbonate solution, using Congo-red as indicator.

Benzyl salicylate, $C_6H_4(OH).COO(C_7H_7)$, is obtained by heating benzyl chloride with a metallic salicylate to 130°–140°. It is a liquid without odour, b. p. 208°, and has been suggested as an external remedy.

Phenyl Salicylate, Salol, $C_6H_4(OH).CO.O.C_6H_5$.—This substance is now manufactured by heating the product of the action of carbon dioxide on sodium phenoxide with phosphorus oxychloride or pentachloride, when phenyl salicylate and metaphosphate and sodium

chloride result. Phosgene (carbonyl chloride) may be substituted for phosphorus pentachloride (*J. Soc. Chem. Ind.*, 1886, **5**, 677).

Phenyl salicylate crystallises in rhombic prisms, m. p. 42° to 43°. It usually occurs as a white crystalline powder of very faint aromatic odour, but the dilute alcoholic solution has a smell resembling that of wintergreen oil, probably owing to the formation of traces of ethyl salicylate. It is almost tasteless, and nearly insoluble in water, but dissolves in alcohol, ether, chloroform, light petroleum, and liquefied carbolic acid.

The alcoholic solution of salol is coloured violet by ferric chloride, whilst bromine gives a precipitate in the form of long needles, consisting of a bromo derivative,[1] crystallising from alcohol in silky needles which melt at 98.5°. When boiled with sodium hydroxide, salol is readily saponified, and the solution when acidified with hydrochloric acid gives an odour of phenol and a copious precipitate of salicylic acid, which after filtration and washing with cold water gives with hot water a solution rendered violet by ferric chloride.

Salol should not redden moistened litmus-paper; and when shaken with 50 parts of water should yield a filtrate which is not rendered violet on addition of 1 drop of ferric chloride nor give any immediate turbidity on adding silver nitrate or barium chloride.

Salol is employed in medicine as a substitute for metallic salicylates and wintergreen oil. Being insoluble, it passes unchanged through the stomach, but in the duodenum is decomposed into phenol and salicylic acid, and these products can be detected in the urine, which is usually very dark in colour. As an antipyretic, antiseptic, and antirheumatic, salol possesses properties of value. When applied externally it has no corrosive action, and its lower m. p. gives it some advantages over salicylic acid.

Salol is sometimes employed in skin and nasal diseases as a substitute for iodoform. When melted with camphor (65:84) it forms a permanent liquid, suitable for this purpose.

A 5% solution of salol in weak alcohol, flavoured in various ways, is employed for mouth-washes, dentifrices, toilet-powders, etc.

Estimation.—For the estimation of salol Squire and Caines (*Pharm. J.*, 1905, [iv], **20**, 720) recommend the following process: 0.5

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[1] The formula of this derivative is given by some authorities as $C_{13}H_9O_3Br$, but seeing that salicylic acid and phenol are both converted by excess of bromine into the compound $C_6H_2OBr_4$, the alleged composition appears highly improbable. Tribromophenol has m. p. 96°.

grm. of the sample is weighed into a flask, treated with 5 c.c. of N-sodium hydroxide solution and 10 c.c. of water, and the ester saponified by heating on a water-bath. The excess of alkali is determined by titration with $N/10$ sulphuric acid. A blank experiment is made by treating 5 c.c. of the N-sodium hydroxide solution in the same way and titrating with the same acid. The difference in volume of acid required in the 2 cases is calculated into salol, 1 c.c. of $N/10$ acid representing 0.021408 grm. of the latter substance. The liberated phenol has no effect on the titration if phenolphthalein is used as indicator.

Telle's method (page 482) for the estimation of salicylic acid may be applied to salol after saponification with boiling aqueous sodium hydroxide. 1 molecule of salol requires 5 molecules of bromine. For the estimation in surgical dressings, the latter are extracted with alcohol (*J. Pharm. Chim.*, 1901, [vi], **14**, 289).

Beythien and Atenstadt (*Zeitsch. Nahr. Genussm.*, 1907, **14**, 392) have described a method of estimating salicylic acid, menthol, phenol, salol, and menthyl salicylate in mouth-washes, etc. This depends on the extraction of the salicylic acid with sodium hydrogen carbonate, and then the phenol with sodium hydroxide solution. The undissolved mixture of menthol, menthyl salicylate, and salol, is saponified, the total menthol separated by its insolubility in alkalis and the salicylic acid and phenol estimated in the alkaline aqueous liquid.

Chlorsalol, or chlorophenyl salicylate, $C_6H_4(OH).COO-(C_6H_4Cl)$, exists in 2 modifications. *o*-Chlorophenyl salicylate forms colourless crystals melting at 55° and has been used in surgery as an antiseptic. The *p*-modification melts at 72°, is insoluble in water, but soluble in alcohol, and in doses of 4 to 6 grm. daily has been used internally as a substitute for salol.

A substance analogous to salol may be obtained by substituting resorcinol for phenol. By heating a mixture of sodium salicylate and cresylate with phosphorus oxychloride, the salicylate corresponding to *o*-, *m*-, or *p*-cresol is obtained according to the modification of cresol employed. The products are termed "*Cresalols*," and have been employed as dusting powders and substitutes for salol.

Alphol and betol (or *Salinaphthol*) are the commercial names of compounds obtained by the action of sodium salicylate on α- and β-naphthol, respectively, in the presence of phosphorus oxychloride. Betol, which is the preferable isomeride, is used as an intestinal antiseptic

in cases of ague and articular rheumatism. It is tasteless and odourless, with a m. p. of 95°. It is almost insoluble in water, but dissolves readily in boiling alcohol and ether.

According to Dragendorff (*Arch. Pharm.*, 1895, **233,** 612), the sulphuric acid solution of betol, when treated with a crystal of chloral hydrate gives an orange colour which changes to reddish-violet and then to red with a green fluorescence (distinction from alphol).

ANHYDRIDES OF SALICYLIC ACID.

Salicylic Anhydride or Di-salicylic Acid,

$$O[C_6H_4CO_2H]_2,$$

results from the action of phosphorus oxychloride on sodium salicylate, and is also formed by the prolonged heating of salicylic acid with acetyl chloride. It is amorphous, soluble without decomposition in cold sodium carbonate solution, but converted into salicylic acid by boiling with alkali hydroxides. It gives no colouration with ferric chloride.

$$\text{Salicylide; Tetrasalicylide,} \quad \begin{vmatrix} O.\ C_6H_4.\ CO_2.\ C_6H_4CO \\ C\ O.\ C_6H_4O.\ CO.\ C_6H_4O \end{vmatrix}.$$
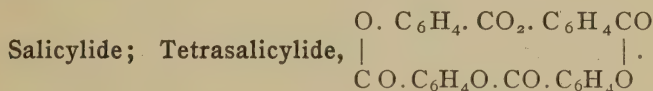
This substance, m. p. 260°, is formed, together with a polymeride, m. p. 325°, when a solution of salicylic acid in xylene is treated with phosphorus oxychloride. The 2 compounds are separated by boiling chloroform, with which the salicylide forms a compound of the formula $(C_7H_4O_2)_4,2CHCl_3$, which crystallises in fine quadratic octahedra containing 33% of loosely combined chloroform. It has been utilised for the preparation of pure chloroform (Anschütz, *Annalen*, 1893, **273,** 94). A similar compound can be obtained from *o*-cresotic acid.

Disalicylide, $(C_6H_4CO_2)_2$, has been described by Einhorn and Pfeiffer (*Ber.*, 1901, **34,** 2951).

HYDROXY-BENZALDEHYDES, $C_7H_6O_2$.

o-**Hydroxy-benzaldehyde,** $C_6H_4(OH)^1.(CHO)^2$, originally known as *salicylous* or *spiroylous acid*, is the aldehyde of salicylic acid, to which it bears the same relation as ordinary aldehyde does to acetic acid. It occurs in the essential oils of the different varieties of *Spiræa*, and likewise in the oil of *Crepis fœtida*. Salicylic aldehyde is also obtained by the oxidation of its alcohol, *saligenol,*[1] or of those glucosides which

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[1] SALIGENOL, saligenin, or ortho-hydroxy-benzyl alcohol, $C_6H_4(OH).CH_2OH$, is described at length under "Salicin," Vol. 7.

yield that substance on hydrolysis, such as salicin and populin.   For the method of synthesis, see Tiemann and Reimer (*Ber.*, 1876, **9**, 824).

.When prepared synthetically, salicylic aldehyde is usually contaminated with the corresponding *p*-aldehyde, from which, however, it is easily separated by distillation in a current of steam, in which the *o*-compound is easily volatile, whereas the *p*-substance is not.

Salicylic aldehyde is a colourless oily liquid, of pleasant aromatic odour, resembling that of oil of meadowsweet (*Spiræa ulmaria*).   It has a sp. gr. of 1.1731 at 13.5°, and b. p. 196.5°.   It is fairly soluble in water, easily so in alcohol and ether, and is readily extracted from its aqueous solutions by the last-named solvent.   Salicylic aldehyde combines with hydrogen sulphites of the alkalis to form crystalline compounds, decomposed by dilute acids with the re-formation of the aldehyde.   On oxidation salicylic aldehyde yields salicylic acid, and like the latter substance, its aqueous solutions yield a deep violet colour with ferric chloride.   Like all *o*-hydroxy-aldehydes, it colours the skin a deep yellow.   Its acid characters are so pronounced that it dissolves in solutions of alkali hydroxides to form crystalline compounds, and even decomposes carbonates.

Towards phenolphthalein and Poirrier's blue it reacts as a monobasic acid.   In doses of 0.1 to 0.5 grm. salicylic aldehyde has been employed as an internal antiseptic and diuretic.

p-**Hydroxy-benzaldehyde,** $C_6H_4(OH)^1.(CHO)^4$, is isomeric with salicylic aldehyde.   Its methyl ether is the well-known *anise aldehyde*, or *p*-methoxy-benzaldehyde, $(CH_3O)^1.C_6H_4.(CHO)^4$, which is known in commerce as "*aubèpine*" or "artificial hawthorn." It forms the basis of many perfumes, especially of that known as "new-mown hay."   It results from the oxidation of several essential oils, such as aniseed and fennel, which contain anethole, and exists therein in greater or less quantity according to the age of the oils. Anisaldehyde can also be prepared synthetically.   It is an aromatic oil of sp. gr. 1.123 at 18° and b. p. 248°.   On oxidation it yields *anisic acid* (page 507).

DERIVATIVES OF SALICYLIC ACID.

In addition to its salts, esters, etc., already described, the derivatives of salicylic acid described in the following tables are of practical interest.   Their chief applications are as antiseptics and anti-rheumatics.

DERIVATIVES OF SALICYLIC ACID.

Chemical nature	Formula	Commercial name	M. p., °	Solubility in:			Colouration with ferric chloride	Therapeutic applications	Dose
				Water	Alcohol	Ether			
Di-iodo-salicylic acid.	$C_6H_3I_2(OH).COOH$	....	220 to 230	Sparingly	Readily	Readily.	......	Analgesic, antithermic, and antiseptic.	1.5 to 4.0 grm.
Sodium di-iodo-salicylate.	$C_7H_3O_3I_2Na + 2.5H_2O$	....	......	1 : 50	....	......	......		0.5 to 1.0 grm.
Methyl di-iodo-salicylate.	$C_7H_3O_3I_2.CH_3$	Sanoform.	110	....	Hot, 1:10.	Sol.	......	Desiccant for wounds and ulcers. Substitute for iodoform.	External use.
Di-thio-salicylic acid (No. 1 and No. 2).	$(C_7H_5O_2)_2.S_2$	....	......	......	......	......	......	Substitutes for iodoform.	External use.
Sodium di-thio-salicylate (No. 1).	$(C_7H_4O_2Na)_2S_2$	Dithion.	......	Sol......	......	......	......	Antiseptic; remedy for foot-and-mouth disease.	External use.
Sodium di-thio-salicylate (No. 2).			......	Hygroscopic.	......	......	......	Antiseptic; remedy for muscular rheumatism and rheumatic fever.	0.2 to 1.0 grm.
Basic bismuth di-thio-salicylate.	....	Thioform	......	Insol.	......	......	......	In diseases of eye, ear, nose and throat; and in veterinary medicine as substitute for iodoform in treatment of eczema, erysipelas, etc.	External use.

DERIVATIVES OF SALICYLIC ACID.—(Continued.)

Chemical nature	Formula	Commercial name	M. p., °	Solubility in:			Colouration with ferric chloride	Therapeutic applications	Dose
				Water	Alcohol	Ether			
Salicyl-sulphonic acid	$C_6H_3.(SO_3H).(OH).$ COOH	Sulpho-salicylic acid.	120	Readily.	Sol.	....	Violet.	In articular rheumatism; valuable reagent for proteids.	....
Sodium sulpho-salicylate.	$C_6H_3.(SO_3Na).(OH)$ COOH	....	....	Readily.	Insol.	Insol.	....	Internal antiseptic; substitute for salol.	....
o-Amido-salicylic acid.	$C_7H_5O_3.(NH_2)$	....	....	Cold, insol.; hot, sparingly.	Insol.	Insol.	Cherry-red colour to brown-black ppt.	In articular rheumatism.	0.25 to 0.5 grm.
Methyl-p-amido-m-hydroxy-benzoate.	$C_7H_3O_3(NH_2).(CH_3)$	Orthoform.	120	Sparingly	....	....	Brown.	Antiseptic and local anesthetic	External use and internally, 0.5 to 1.0 grm.
Sodium salt of methyl-p-amido-m-hydroxy-benzo-sulphonate.	$C_7H_3O_3(SO_3Na).(N-H_2).(CH_3)+H_2O$	Sulphonated orthoform.	269	Readily.	....	....	....	Substitute for orthoform.	....
Methyl-m-amido-p-hydroxy-benzoate	$C_7H_3O_3.(NH_2).(CH_3)$	New orthoform.	142	Somewhat sol.	....	....	Green colour and dirty green ppt.	Substitute for orthoform.	....

DERIVATIVES OF SALICYLIC ACID.—(*Continued.*)

Chemical nature.	Formula.	Commercial name	M. p., °	Solubility in: Water	Alcohol	Ether	Colouration with ferric chloride	Therapeutic applications.	Dose
Acetyl-salicylic acid...	$C_6H_4.(O.C_2H_3O).C-OOH$	Aspirin.	135	Insol.	Sol. (1:15)	....	no colouration	Anti-rheumatic; substitute for salicylates.	....
Acet-amido-ethyl salicylic acid.	$C_6H_3.(O.C_2H_5)(NH.CO.CH_3)COOH$	Benzacetin.	189 to 190°	Insol.	....	....	......	Anti-neuralgic.	0.5 to 1.0 grm.
Acetyl-p-amido-phenyl salicylate.	$C_6H_4(OH).CO_2.C_6H_4-[NH(COCH_3)p]$	Salophen.	187 to 188	Insol.	Sol.	Sol.	Violet.	Substitutes for salol; in rheumatism, neuralgia and influenza.	1 to 2 grm.
Acetonyl salicylate...	$C_6H_4(OH).CO_2.(CH_2.-.CO.CH_3)$	Salacetol; Salantol.	71	Almost insol.	Cold slightly; hot, readily	Hot, readily.	......		2 to 3 grm.
Condensation product of salicylic and gallic acids	$C_6H_4(OH).CO.O.C-O.C_6H_2.(OH)_3$	Salitannol.	210	Insol.	Sparingly.	Insol.	......	Antiseptic; substitute for salol	Chiefly external use.
Condensation product of boric and salicylic acids	$B.OH.(O.C_6H_4.CO-OH)_2$	Boro-salicylic acid.	......	....	....	....	......	Antiseptic.	External use.
Mixture of boric acid and sodium salicylate	....	Borsalyl; Borosalyl.	......	Sol.	....	....	......	Antiseptic.	External use.
Salicylamide.........	$C_6H_4.(OH).CO.(N-H_2)$	....	138	1 : 250	Sol.	Sol.	......	Substitute for salicylates.	0.1 to 0.3 grm.
Salicyl-a-methyl-phenylhydrazone.	$C_6H_5.(CH_3).N.N.CH.(C_6H_4).OH:$	Agathin; Cosmin.	74	Insol.	Sol.	Sol.	......	Anti-neuralgic and anti-rheumatic.	0.12 to 0.5 grm.

Salicyl-sulphonic Acid, $C_6H_3(SO_3H)(OH).COOH$.—This compound, sometimes termed sulpho-salicylic acid, is prepared by heating salicylic acid with twice its weight of sulphuric anhydride at 100°, until dissolved. On cooling and standing, brownish crystals of the sulphonic acid separate, and may be purified by crystallisation from boiling water.

Sulphosalicylic acid forms long, thin needles, m. p. 120°, which are very soluble in water. They are coloured a deep reddish-violet by ferric chloride. On fusing sulphosalicylic acid with potassium hydroxide, phenol and salicylic acid are produced, without any dihydroxybenzene being formed.

Sulphosalicylic acid is a delicate reagent for albumin and is a useful precipitant of all varieties of proteids in urine.[1]

Sodium sulphosalicylate, $C_6H_3(OH).(COOH).SO_3Na$, is obtained by partially neutralising sulphosalicylic acid with sodium carbonate, so as to saturate the sulphonic group only. It is a readily soluble salt, which has found application as an internal antiseptic. It is stated to possess all the advantages of salol, without having the tendency of the latter to liberate free phenol in the system.

Acetyl-salicylic acid is sold commercially under the name "aspirin." It is prepared by heating salicylic acid with acetyl chloride or acetic anhydride, and recrystallising the product. The m. p. usually given is 135°, but the present writer has observed 136 to 137°.

When the pure acid is shaken with water and the liquid filtered the filtrate gives no colouration with ferric chloride, but if heated with water it is partly hydrolysed and the solution then gives the violet colour characteristic of salicylic acid.

It is used medicinally instead of salicylic acid, over which it is said to have some advantages.

Estimation.—Acetyl-salicylic acid reacts towards cold potassium hydroxide solution as a monobasic acid, when phenolphthalein is used as indicator. Since 1 grm. requires 55.54 c.c. of decinormal alkali, whilst the same weight of salicylic acid requires 72.44 c.c., every 1% of the latter acid present as impurity raises the volume of alkali required to neutralise 1 grm. 0.169 c.c. above the former figure

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[1] A few crystals of the reagent should be added to a small quantity of the clear urine and the liquid agitated, when a turbidity or actual precipitate will be formed if a proteid be present. The precipitate produced by albumins and globulins is not affected by heat, whereas that due to albumoses and peptones dissolves, reappearing as the liquid cools. No normal or abnormal constituent of urine other than proteids is precipitated by the reagent, but these are very completely separated. 1 part of egg albumin in 20,000 of water can be detected by the test (Roch, *Pharm. Centr.*, 1889, **30**, 549).

(55.54). If the neutralised liquid is boiled for a few minutes with excess of the decinormal alkali, an equal volume to that used for neutralisation will be absorbed if the substance is pure, whilst if salicylic acid is present a lesser volume will be required.

The titration is best effected as follows: 1 grm. of the sample is weighed into a 200 c.c. flask, dissolved in a small quantity of alcohol, a drop of phenolphthalein solution added, and titrated as quickly as possible with $N/10$ potassium hydroxide solution, the volume required being noted. To the liquid a volume of $N/10$ alkali about 5 c.c. in excess of that already used, is added, the solution boiled for 5 minutes, and the excess of alkali titrated with $N/10$ acid. The total volume of $N/10$ alkali required will be double that used in the cold neutralisation if the sample is free from salicylic or any other acid. If the sole impurity is salicylic acid, every 1% present will depress the total volume of alkali absorbed by 1 grm., 0.38 c.c. below 111.08 c.c., the volume required by the pure acid. 1 c.c. of cold $N/10$ potassium hydroxide solution neutralises 0.0180064 grm. whilst the same volume of the boiling alkali reacts with 0.0090032 grm. of acetylsalicylic acid.

Since cold potassium hydroxide solution slowly hydrolyses acetylsalicylic acid, the cold titration must be effected quickly or erroneous results will be obtained.

Phenyl acetylsalicylate, obtained by acetylating salol has been introduced commercially under the name "vesipyrin" (Zernik, *Apoth. Zeit.*, 1907, **22,** 152). It is a white, almost tasteless powder, m. p. 97°, insoluble in water, but readily soluble in alcohol and ether. The alcoholic solution gives no colouration with ferric chloride. It is easily saponified with boiling aqueous alkalis.

HOMOLOGUES OF SALICYLIC ACID.

A large number of acids are known of the empirical formula $C_8H_8O_3$. Thus:

(A.) Phenyl-glycollic acids.   Mandelic acid. $C_6H_5.CH < ^{CO_2H}_{OH}$

(B.) Hydroxy-methyl-benzoic acids . . . . $C_6H_4 < ^{CO_2H}_{CH_2OH}$

(C.) Methoxy-benzoic acids (*e. g.*, anisic acid) $C_6H_4 < ^{CO_2H}_{OCH_3}$

(D.) Hydroxy-phenylacetic acids . . . . $C_6H_4 < ^{CH_2CO_2H}_{OH}$

(E.) Hydroxy-toluic acids (*e. g.*, cresotic acids) $C_6H_3Me < ^{CO_2H}_{OH}$

10 chemical modifications of hydroxy-toluic acid exist, and 3 each (ortho-, meta-, and para-) of hydroxy-phenylacetic, methoxy-benzoic, and hydroxy-methylbenzoic acids are known. The hydroxy-phenyl-acetic acids are analogues of hydracrylic acid, whilst mandelic acid corresponds to ordinary lactic acid.

The hydroxy-methylbenzoic acids are alcohols, whereas the hydroxy-phenylacetic and hydroxytoluic acids have a phenolic constitution.

Mandelic acid, $C_6H_5.CH(OH).COOH$, contains an asymmetric carbon atom, and hence, like lactic acid, occurs in 3 sterioisomeric forms, 2 of which exhibit optical activity in opposite directions ($[a]_D =$ 158° at 20°), whilst the third or racemic variety is obtainable by mixing the 2 optically active isomerides in equal proportions.

Inactive mandelic acid crystallises in orthorhombic prisms, m. p. 118°, readily soluble (16 : 100) in cold water, alcohol, and ether. On oxidation by nitric acid, mandelic acid first yields *benzoylformic* and ultimately *benzoic acid*.

The optically-active mandelic acids behave like the inactive acid with reagents, but melt at 133°. The lævo-rotatory modification occurs naturally, and may be obtained by digesting amygdalin with fuming hydrochloric acid for some hours at 100°. Fermentation of the ammonium salt of the inactive acid with *Penicillium glaucum* destroys the lævo-acid and leaves the dextro-modification; whereas *schizomycetes* destroy the dextro-acid and leave the lævo-rotatory modification. The 2 active modifications can be prepared from the inactive acid by converting it into a cinchonine salt and adding a crystal of cinchonine dextro-mandelate, when the salt of the dextro-acid crystallises out, leaving that of the lævo-acid in solution.

Hydroxymethyl-benzoic Acids, $C_6H_4(CH_2OH).COOH.$—The ortho-modification melts at 120° (with simultaneous conversion into the anhydride, "phthalide"), the meta- at 180°, and the para-acid at 181°.

·*o*-**Hydroxymethyl-benzoic acid** is obtained by the action of alka-lies on its anhydride, *phthalide*. On acidifying the solution the acid is precipitated as a powder slightly soluble in cold water but readily in alcohol. When heated to its m. p., the acid is converted into its anhydride, which is also formed by simply boiling the acid with water.

o-**Hydroxymethyl-benzoic Anhydride,** or *Phthalide,* $C_6H_4 \begin{matrix} CO \\ CH_2 \end{matrix} O.$

—This compound is formed as stated above, and may be obtained by

a variety of synthetic reactions (Wislicenus, *Ber.*, 1884, **17**, 2181). It crystallises from boiling water in needles which have an odour like that of cinnamon. Phthalide has m. p. 73° and b. p. 290°. It does not combine with hydrogen sulphites nor reduce ammonio-silver nitrate, and it yields no compound with hydroxylamine. Phthalide is oxidised to phthalic acid by treatment with alkaline permanganate. It is reduced to *o*-toluic acid by heating with hydriodic acid and phosphorus, and yields *o*-toluic acid and a little *o*-xylene when heated with zinc dust.

Methoxybenzoic Acids, $C_6H_4(OCH_3).COOH.$ — The 3 modifications of this compound have the following characters:

	COOH:OCH$_3$	M. p.,°	B. p.,°	Crystalline form
Ortho-acid. Methyl-salicylic acid.	1 : 2	98.5°	. . . .	Monoclinic tablets and prisms.
Meta-acid	1 : 3	107°	. . . .	White needles.
Para-acid. Anisic acid.	1 : 4	184°	275°–280°	Monoclinic prisms or needles.

o-**Methoxybenzoic acid or methyl-salicylic acid** is isomeric with methyl salicylate. It crystallises from hot water in large monoclinic tablets, and from alcohol in prisms, m. p. 98.5°, and decomposing above 200° into *anisole*, $C_6H_4.OCH_3$, and carbon dioxide. When heated with concentrated hydrochloric or hydriodic acid, methyl-salicylic acid yields salicylic acid and methyl chloride or iodide.

Methyl-salicylic acid gives no violet colouration with ferric chloride.

Anisic acid, $C_6H_4(OCH_3).COOH$, has the constitution of *p-metnoxy-benzoic acid*. It was first obtained in 1839 by the oxidation of anise oil, and subsequently by similar treatment from the oils of tarragon, fennel, star-anise, etc., all of which contain *anethole* or anise-camphor, $C_6H_4(OCH_3)C_3H_5$, which yields anisic acid on oxidation.

Anisic acid may also be prepared by several synthetical reactions.

Anisic acid forms long monoclinic needles or prisms, m. p. 184°, b. p. 280°. It is soluble in about 2,500 parts of cold water, tolerably soluble in boiling water and readily in alcohol.

When heated with hydriodic or concentrated hydrochloric acid, or when fused with potassium hydroxide, anisic acid is converted into

p-hydroxybenzoic acid. When distilled with baryta, it is decomposed into anisole and carbon dioxide.

The sodium salt and phenyl ester of anisic acid are employed in the treatment of neuralgia and rheumatism.

Hydroxy - phenyl - acetic Acids, $C_6H_4(OH).CH_2.COOH.$ — The ortho-modification melts at 144°–145°, the meta- at 129°, and the para- at 148°. The last-named has been found in urine, and is formed in the putrefaction of albumin and synalbin. All 3 isomer-ides give a violet colouration with ferric chloride. When heated with lime they yield carbon dioxide and the corresponding isomeride of cresol, $C_6H_4(OH).CH_3$.

Hydroxy-toluic Acids.—10 modifications of hydroxy-toluic acid are possible and all have been prepared. The following arrangement shows the m. p. of these isomerides. Thus the acid having the COOH, OH, and CH$_3$ groups in the positions 1 : 2 : 3 melts at 163°, whilst when the methyl group occupies the para-position, the other groups remain-ing as before, the compound melts at 177°.
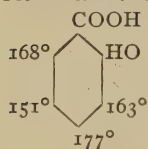
Ortho-derivatives	Meta-derivatives	Para-derivatives
COOH	COOH	COOH
168° ⟋ ＼ HO	183° ⟋ ＼ 146°	(177°) ⟋ ＼ 177°
151° ＼ ⟋ 163°	210° ＼ ⟋ OH	(173°) ＼ ⟋ 173°
177°	207°	OH
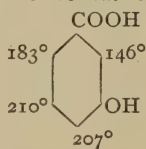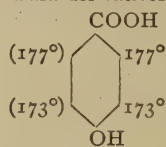
Those hydroxy-toluic acids which have the hydroxyl group in the *ortho*-position (1:2) in reference to carboxyl are true homologues of salicylic acid, and are known as *homosalicylic* or *cresotic acids*.[1] They give a violet colouration with ferric chloride, dissolve with facility in cold chloroform, and volatilise readily in a current of steam. The cresotic acids are liable to occur as objectionable impurities in commer-cial salicylic acid (see page 472).

Of the 4 acids having the carboxyl and hydroxyl groups in the *meta*-position (1 : 3) relatively to each other, 3 give pale brown precipitates with ferric chloride, soluble more or less readily in excess of the reagent to dark brown solutions. The 1 : 3 : 4 acid gives no reaction with ferric chloride. The meta acids are not attacked by heating with concentrated hydrochloric acid at about 200°, but yield cresols when

[1] Some chemists in expressing the constitution of the hydroxy-toluic acids, assign a constant position 1 to the methyl-group, following with the hydroxyl and carboxyl groups in the order named. Such a plan materially alters the nomenclature of the acids, and fails to exhibit the analogy of properties and reactions set forth in the text.

heated with lime. They are volatile with difficulty or not at all ($1:3:5$ acid) in a current of steam.

The 2 homologues of p-hydroxybenzoic acid crystallise in small needles containing $1/2H_2O$, which become anhydrous at $100°$. They volatilise more or less in a current of steam, but give no reaction with ferric chloride and are not soluble in cold chloroform.

The table on the following page exhibits the leading characters of the isomeric hydroxy-toluic acids:

Cresotic acid, $C_6H_3(CH_3)(OH).COOH$, may be prepared from cresol by Kolbe's method for the manufacture of salicylic acid from phenol, the modification of cresotic acid obtained depending on the isomeride of cresol employed for the process. It is to the presence of cresols in the carbolic acid employed in Kolbe's process that the contamination of commercial salicylic acid by the isomeric cresotic acids is due (page 472). The 3 isomerides of cresotic acid present a close resemblance to salicylic acid and to each other, but differ in their m. p., therapeutic action and the modification of the cresol yielded on heating under pressure with hydrochloric acid or distillation with lime.

According to M. Charteris (*Pharm. J.*, 1890, [iii], **21**, 436), m-cresotic acid is devoid of physiological action, but both the o- and p-modifications possess marked toxic properties. Charteris found p-cresotic acid to produce marked paralytic symptoms in rabbits when injected hypodermically, the effect becoming more marked when the poison was given in conjunction with salicylic acid, 10 grains of the mixture causing convulsions and death.

The foregoing conclusions of Charteris have had grave doubt thrown on them by the observations of others. Thus Egasse has drawn attention to the advantages of p-cresotic acid as an antipyretic. Demme regards it as inferior to salicylic acid as an antipyretic, but free from some of the objections to the latter, being better tolerated by the digestive organs. Demme considers p-cresotic acid the most effectual and least objectionable of the 3 isomerides. m-Cresotic acid he regards as less active, whilst o-cresotic acid possesses decided toxic properties, causing paralysis of the cardiac muscle. According to Demme, also, the observed ill effects are attributable to the presence of o-cresotic acid in the preparations used. Sodium p-cresotate may be taken to the extent of 3 to 4 grm. without any ill effect resulting. It did not influence the temperature or occasion gastric disturbance (*Bull. Therap.*, 1892, **122**, 85; abst. *Pharm. J.*, 1892, [iii], **22**, 694).

ISOMERIC HYDROXY-TOLUIC ACIDS.

Acid. COOH:OH:Me	M. p., °	On heating with hydrochloric acid	Reaction with ferric chloride	Solubility in cold chloroform	Crystalline form	M. p. of methyl ethers	Observations
Ortho-.							
1:2:3	163	o-cresol at 210°	Deep violet colour	Readily	Long flat needles or rhombic prisms.	85°	o-cresotic acid; poisonous.
1:2:4	177	m-cresol at 170°.	Deep violet colour	Moderately.	Hard white needles or prisms	103°	m-cresotic acid.
1:2:5	151	p-cresol at 180°	Violet-blue colour	Readily	Long needles and rhombic prisms.	67°	p-cresotic acid; gives p-cresol on heating with lime.
1:2:6	168	m-cresol at 200°	Blue-violet colour	Readily	Long needles....		....
Meta-.							
1:3:2	145°–146°	Not attacked at 210°.	Yellowish-brown colour.	Slight........	Long vitreous needles.	146°	Gives o-cresol when heated with lime.
1:3:4	207	Not attacked at 270°	No reaction....	Insoluble....	Long needles....	156°	Gives o-cresol when heated with lime.
1:3:5	208	Not attacked at 230°.	Fawn ppt. dissolving in excess with dark brown colour.	....	Stellate groups of needles.	93°	Symmetrical hydroxytoluic acid. Gives m-cresol when heated with lime. Not volatile with steam.
1:3(5)6(2)	183–184°	Not attacked at 220°.	Light brown ppt. sol. in much water.	Nearly insoluble.	Prisms and needles.		....
Para-.							
1:4:2(6)	177	m-cresol at 200°.	None...........	Insoluble...	Small needles containing ½H_2O.	176°	....
1:4:3(5)	173	o-cresol at 180°.	None...........	Insoluble ..	Small needles containing ½H_2O.	193°	....

A solution of cresotic acid has received application as a beating liquid in tanneries. It is stated to have the advantage over other acids of exerting an antiseptic action on the skins, and so preserving instead of destroying them (J. Hauff, *J. Soc. Chem. Ind.*, 1889, **8**, 974). As it rapidly and easily dissolves the lime salts, it softens and swells the hides in a very satisfactory manner.

DIHYDROXYBENZOIC ACIDS AND THEIR ALLIES.

By the substitution of 2 hydroxyl-groups for 2 of the remaining hydrogen atoms of the benzene-nucleus in benzoic acid, a series of dihydroxyphenyl-carboxylic or dihydroxy benzoic acids are obtained, of which protocatechuic acid is the type.

The dihydroxybenzoic acids may be obtained (among other reactions) by heating the corresponding dihydroxybenzenes (hydroxyphenols) with solutions of alkali carbonates, the reaction occurring with much greater facility than the formation of salicylic acid by Kolbe's process (page 470). By further heating, the dihydroxybenzoic acids split up into the corresponding hydroxyphenols and carbon dioxide.

ISOMERIC DIHYDROXYBENZOIC ACIDS. $C_6H_3(OH).(OH).COOH$.

	Acid	COOH : OH : OH	M. p., °	Colour with ferric chloride	Phenolic product, on heating.
o-hydroxyphenyl-carboxylic acids	Protocatechuic.	1 : 3 : 4	194°–195°	Green.	Catechol.
	Catechol-carboxylic.	1 : 2 : 3	204°	Blue.	Catechol.
	α-Resorcylic	1 : 3 : 5	222 (233)	No colour.	Resorcinol.
	β-Resorcylic.	1 : 2 : 4	213	Dark-red.	
m-hydroxyphenyl-carboxylic acids ...	γ-Resorcylic.	1 : 2 : 6	148 (decomp.)	Violet; blue with excess.	Resorcinol. Resorcinol.
p-hydroxyphenyl-carboxylic acid	Gentisinic, or hydroxysalicylic.	1 : 2 : 5	200	Blue.	Quinol.

Protocatechuic acid. Ortho-dihydroxybenzoic acid.

$$C_7H_6O_4; \; i.\, e.,\; C_6H_3 \diagdown \begin{matrix} (1)COOH \\ (3)OH \\ (4)OH \end{matrix}$$
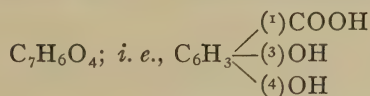
Protocatechuic acid occurs naturally in the fruit of *Illicium religiosum*. It results from the fusion of various organic substances with

alkali hydroxides. Catechin and maclurin by similar treatment yield phloro-glucinol. Many resins give *p*-hydroxybenzoic acid in addition, whilst gum benzoin gives protocatechuic and benzoic acids. The largest yield of protocatechuic acid is stated to be obtainable from gum kino (*Annalen*, 1875, **177,** 188). It may be prepared synthetically by heating catechol to 130° with a solution of sodium or ammonium carbonate. On dry distillation or when heated to 330° to 350° with potassium or sodium hydroxide, the reverse action occurs, the protocatechuic acid splitting up into catechol and carbon dioxide.

Protocatechuic acid forms thin monoclinic prisms or tufts of needles containing one molecule of water, which is lost at 100°. It melts when quite anhydrous at 194° to 195°[1] and at a higher temperature is resolved into carbon dioxide and catechol, $C_6H_4(OH)_2$. Protocatechuic acid dissolves in 53 parts of cold water, and in 3.5 parts at 80°. It is very soluble in alcohol, less so in ether, and almost insoluble in benzene, even when boiling. It is extracted from its aqueous solution by agitation with ether or light petroleum.

Reactions.—An aqueous solution of protocatechuic acid is coloured an intense bluish-green by ferric chloride (avoiding excess), the colour being changed to blue and afterwards to dark red on adding a very dilute solution of sodium carbonate. A neutral solution of a protocatechuate gives a violet colouration with ferrous sulphate.

Protocatechuic acid gives a white precipitate with lead acetate, and reduces ammonio-nitrate of silver when heated, but has no effect on Fehling's solution.

On boiling protocatechuic acid with aqueous arsenic acid it yields *diprotocatechuic acid,* $C_{14}H_{10}O_7$, a substance closely resembling digallic acid (tannin), but giving a green colouration with ferric chloride.

The salts of protocatechuic acid are unimportant, but the esters, vanillic acid, piperonylic acid, and veratric acid have some interest (page 513).

Estimation.—Imbert stated (*Compt. Rend.*, 1900, **130,** 37) that protocatechuic acid is monobasic towards phenolphthalein. According to Massol, however, the acid requires 1.5 molecules for neutralisation (*Bull. Soc. chim.*, 1900, [iii], **23,** 331). But the acid used by the latter author was yellow, and had m. p. 199° (instead of 194–195°), and Imbert, on repeating his experiments, confirmed his original

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[1] This seems to be the correct m. p., but Hlasiwetz gives 199° and Schmidt and Barth give 194°.

statement (*Bull. Soc. chim.*, 1900, [iii], **23**, 832). The end-point is somewhat obscure. Towards Poirrier's blue protocatechuic acid is dibasic.

Homologues of Protocatechuic Acid.—Besides the important class of tannins giving green colourations with ferric salts (Vol. 5), the following homologues and derivatives of protocatechuic acid have a practical interest:

Name	Formula	M. p., °	Colouration with ferric chloride
Orsellinic acid. Dihydroxy-*o*-toluic acid.	$C_6H_2(CH_3)$⟨$^1CO.OH$, ^2OH, ^4OH⟩	176	Violet.
a-Homoprotocatechuic acid.....	C_6H_3⟨$^1CH_2.CO.OH$, ^3OH, ^4OH⟩	127	Green
iso-Vanillic acid. *p*-Methylprotocatechuic acid.	C_6H_3⟨$^1CO.OH$, ^3OH, $^4O.CH_3$⟩	250	Yellow.
Vanillic acid. *m*-Methylprotocatechuic acid.	C_6H_3⟨$^1CO.OH$, $^3O.CH_3$, ^4OH⟩	207	No colour.
Vanillin. *m*-Methylprotocatechuic aldehyde.	C_6H_3⟨$^1CH.O$, $^3O.CH_3$, ^4OH⟩	80°–81°	Blue.
Piperonylic acid. Methylene-protocatechuic acid.	C_6H_3⟨$^1CO.OH$, ^3O⟩CH_2, ^4O	228	
Piperonal. Methylene-protocatechuic aldehyde.	C_6H_3⟨$^1CH.O$, ^3O⟩CH_2, ^4O	37	
Veratric acid. Dimethylprotocatechuic acid.	C_6H_3⟨$^1CO.OH$, $^3O.CH_3$, $^4O.CH_3$⟩	179	Yellow.

Vanillin. $C_8H_8O_3$; *i. e.*,

CHO

OCH₃

OH
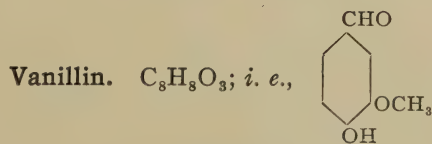
Vanillin is the aldehyde of vanillic or methylprotocatechuic acid. It is the chief odouriferous principle of vanilla pods or *vaniloes*, the fruit of *Vanilla planifolia*, from which it was isolated in 1858. It also occurs in traces in cloves, beetroot, Siam benzoin, asafœtida, and as-

paragus, whilst its presence in the wood of certain trees has been frequently noted.   (See Von Lippmann, *Ber.*, 1904, **37,** 4521.)

Vanilla is the fruit or pod of *Vanilla planifolia*, var. *aromatica*, an orchid grown in Mexico, Bourbon, the Seychelles, Fiji, etc.   Its cultivation has become to a certain extent restricted since vanillin has been produced artificially; but the superior aroma and flavour of the natural product prevent the artificial vanillin from wholly superseding it.[1]

W. Busse (*Arb. Kaiserl. Ges.,* 1898, **15,** 1) found 2.16% of vanillin in German East African vanilla; 1.48% in Ceylon pods; and 1.55 and 2.02% in Tahiti vanilla.   Tiemann and Haarmann (*Ber.,* 1875, **8,** 1115) found in the best Mexican pods 1.69 and 1.86 of vanillin; in Bourbon, 1.91 to 2.90; and in Java pods 2.75% of vanillin.

Busse holds that there is no relation between the proportion of vanillin contained in the fruit and the value of the sample for flavouring purposes, and that the aroma and flavour of vanilla are not wholly due to vanillin.   Tiemann and Haarmann found that on distilling the ethereal extract of vanilla, from which the vanillin has been removed by sodium hydrogen sulphite, an oily substance of very offensive odour remained.   Much less was obtained from Mexican vanilla than from Java or Bourbon pods.

In the variety of West Indian vanilla called *vanillone* the vanillin (from 0.4 to 0.7%) is associated with another substance, which is probably benzaldehyde.   Vanillone has long been used for preparing "essence of heliotrope," but this is now made by adding a small quantity of benzaldehyde (artificial) to artificial vanillin, when, after some time, the mixture acquires the exact odour of the natural white heliotrope.

Some varieties of vanilla contain *vanillic acid*, which was apparently mistaken for benzoic acid by the earlier investigators.

Inferior or exhausted vanilla is occasionally dusted over with crystals of benzoic acid, which gives it the frosted appearance regarded as characteristic of vanilla of good quality.   If a little of the crystalline matter be added to an alcoholic solution of phloroglucinol previously mixed with an equal volume of hydrochloric acid, a magnificent red colour is produced in presence of vanillin.

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[1] The substance to which the odour of vanilla is due does not appear to exist in the fruit when gathered, but is developed during the "curing" operation by a process of fermentation (compare Lecomte, *Comp. rend.*, 1901, **133,** 745).   The greater part of the vanillin is contained in the fruit in the form of a glucoside, from which free vanillin can be obtained by the action of emulsin or dilute acids.

Vanillin is now produced artificially on a considerable scale, by a variety of methods, some of which have proved very lucrative.[1]

Practically the whole of the artificial vanillin of commerce is now made from eugenol, a phenol contained in oil of cloves and oil of cinnamon leaves, by acetylating it with acetic anhydride and oxidising the acetate with potassium permanganate and sulphuric acid (Bertram D. R. P. 63007; Sommer D. R. P. 122851; Schering D. R. P. 82816; etc.).

Vanillin crystallises in stellate groups of colourless needles, melts at 80° to 81°, and sublimes when cautiously heated. It has a pleasant aromatic taste and odour resembling vanilla. Vanillin dissolves sparingly in cold water, more freely in hot, and readily in alcohol and ether.

Commercial vanillin is not infrequently adulterated to a considerable extent (e. g., 50%) with acetanilide (antifebrin), an addition which lowers the m. p. of the sample. The admixture may be detected by heating the substance to 60° with a 5% solution of sodium hydroxide when aniline is formed and may be detected by the usual tests. A quantitative separation of vanillin and acetanilide may be effected by dissolving the mixture in ether and shaking the liquid with a concentrated aqueous solution of sodium hydrogen sulphite, which dissolves the vanillin only. The amount of acetanilide present in vanillin may also be deduced from the nitrogen in the sample (L. F. Kebler, *Amer. J. Pharm.*, 1902, **74**, 12).

Sugar is occasionally met with as an adulterant of vanillin. It may be detected by its insolubility in ether or chloroform.

In America, vanillin is sometimes adulterated with *benzoic acid*, and occasionally that acid simply flavoured with vanillin has been substituted for the latter substance. The 2 substances may be separated by dissolving the sample in ether and shaking the liquid with sodium hydrogen sulphite solution, which will remove the vanillin, leaving the benzoic acid dissolved in the ether.

Kebler has met with vanillin adulterated with or substituted by acetyl-*iso*-eugenol, the direct antecedent of vanillin in its synthetic production from *iso*-eugenol. One adulterated sample contained only a little vanillin, added to give the characteristic odour. Acetyl-*iso*-eugenol melts at 79° to 80°, and vanillin at 80° to 81°. The adulterant was detected by its crystalline form, abnormal solubility in various solvents, and by the presence of the acetyl-group. Strong sulphuric

[1] In 1876, the price of vanillin was fully £10 per ounce. At present it may be bought for 3s. or less.

acid gave a beautiful red colour, whereas a lemon-yellow colour is yielded by pure vanillin. The amount of vanillin was estimated by the Hess and Prescott method (page 519).

Reactions.—Vanillin has the constitution and characters of an aromatic aldehyde. It forms well-defined sulphite compounds, reduces ammoniacal silver solution, and responds to other general reactions for aldehydes. Heated with dilute hydrochloric acid (preferably under pressure to 200°) vanillin is resolved into methyl chloride and protocatechuic aldehyde; and when fused with potassium hydroxide is converted into protocatechuic acid.

By exposing moist and finely pulverised vanillin to the air it is oxidised to vanillic or methylprotocatechuic acid, $C_8H_8O_4$, which crystallises from ether in white laminæ, and gives no colour reaction with ferric chloride.

By reducing vanillin in dilute alcoholic solution with sodium amalgam, vanillyl alcohol, $C_6H_3(OH)(OCH_3),CH_2OH$, is produced, which forms prisms m. p. 115°. Vanillin has an acid reaction and forms salts with bases.

On heating vanillin with hydrochloric acid and phloroglucinol a characteristic red colour is produced.

On rubbing together vanillin, resorcinol, and hydrochloric acid, a deep bluish-violet colouration is observed, which vanishes after a time (Etti, *Monatsh.*, 1882, **3**, 637). A 1% solution of vanillin in hydrochloric acid mixed with an equal volume of sulphuric acid, gives with a few drops of a liquid containing even 0.01% of acetone, a violet colour on heating at 100° for 15 minutes.

If a little thiophene and concentrated sulphuric acid be added to an alcoholic solution of vanillin, the liquid acquires a green to bluish-green colouration (A. Ihl, *Chem. Zeit.*, 1890, **14**, 1707).

Besides its agreeable odour, vanillin is characterised by the bluish-violet colouration produced in its solution on addition of ferric chloride. On heating the liquid, *dehydro-divanillin*, $C_{12}H_4(OH)_2(COH)_2(OCH_3)_2$, separates in fine white needles, m. p. 304°, and sparingly soluble in water, alcohol, ether, chloroform, and benzene, but readily soluble in alkalis (Tiemann, *Ber.*, 1885, **18**, 3493).

A. Stocky (*Zeitsch. Nahr. Genussm.*, 1900, **3**, 233) isolated vanillin from a sample of wine vinegar suspected to contain it, by evaporating a large volume of the liquid to dryness with calcium carbonate, extracting the residue with ether, and evaporating the ethereal solu-

tion. After repeatedly crystallising the residue thus obtained from alcohol it was identified as vanillin by the formation of a metallic mirror with an ammoniacal silver solution, and its reaction with phloroglucinol and hydrochloric acid.

Estimation.—Vanillin may be extracted from aqueous liquid containing it by acidifying and agitating with ether. It may then be separated from many substances simultaneously extracted by agitating the ethereal solution with a semi-saturated solution of sodium hydrogen sulphite.

J. Hanuš has described a method of estimating vanillin based on its conversion into a hydrazone of suitable properties (*Zeit. Nahr. Genussm.*, 1900, **3**, 531).

Owing to the instability of *p*-bromophenyl hydrazine and the interference of foreign substances (especially fats), however, he has abandoned the use of hydrazines in favour of the following process (*Zeitsch. Nahr. Genussm.*, 1905, **10**, 587): The solution of vanillin (approximately 0.25%) is treated with 50% excess of a 2% solution of *m*-nitrobenzoylhydrazide in hot water. The flask containing the mixture is closed with a cork and allowed to stand with occasional shaking for 24 hours, when the smell of vanillin should have disappeared. Vanillin solutions of the above strength are precipitated immediately, but more dilute solutions give no cloudiness until after 5 or 10 minutes. The precipitate is collected on a tared Gooch crucible, washed with cold water until the filtrate no longer reduces ammoniacal silver nitrate solution, and dried for 2 hours at 100 to 105°. After 10 minutes heating at this temperature, the precipitate turns brown and becomes glassy, but at the end of a further 15 minutes it regains its original appearance. The weight of the precipitate multiplied by 0.4829 gives the weight of vanillin.

For the estimation in vanilla, 3 grm. of the powdered sample are extracted for 3 hours with not more than 50 c.c. of ether. The extract is evaporated at 60°, at which temperature no appreciable amount of vanillin is volatilised, the residue dissolved in a small quantity of ether, filtered into a conical flask and the filter washed with ether. The filtrate and washings are evaporated, the residue warmed with 50 c.c. of water to form an emulsion, and precipitated as described above. Before filtration of the precipitate the liquid is shaken with light petroleum to dissolve any fat present, and the solid collected in the Gooch crucible is washed with the same solvent. The method is inap-

plicable in the presence of piperonal or other aldehydes. Hanuš states that his methods are applicable in all cases where an aqueous solution of the vanillin can be prepared, and claims that they have the advantage over Welman's method (titration with alcoholic potassium hydroxide) of being unaffected by the presence of vanillic acid.

A more rapid but less accurate method of estimating vanillin in vanilla is as follows: A known weight (20 to 50 grm.) of the pods should be ground up with sand, and the mixture extracted with ether. The filtered liquid is shaken with a saturated solution of sodium hydrogen sulphite, diluted with an equal volume of water, and the ethereal layer separated. The sulphite solution is then treated with dilute sulphuric acid and the sulphurous acid liberated driven off by passing a current of carbon dioxide or steam. The vanillin is then extracted from the acid liquid by agitating with ether, which is separated, cautiously evaporated, and the residual vanillin weighed.

Certain species of vanilla contain *piperonal* as well as vanillin. No satisfactory method has hitherto been proposed for the separation of these 2 aldehydes, and any process for the estimation of vanillin in presence of piperonal must depend on the reactions of the free hydroxyl-group present in vanillin but not in piperonal. Certain colour-reactions fall under this head, *e. g.*, with mercurous nitrate, *p*-nitrodiazobenzene or ferric salts, but these are hardly applicable for quantitative purposes. Hence J. Hanuš (*Zeitsch. Nahr. Genussm.*, 1900, **3**, 657) recommends the following procedure: A volume of liquid, estimated to contain from 0.02 to 0.15 grm. of vanillin, is placed in an Erlenmeyer flask of 150 c.c. capacity, and 10 c.c. of a 10% solution of platinic chloride added. The volume is then made up to 50 c.c. with water (with more than 0.06 grm. of vanillin it may be made up to 100 c.c. if desired). The flask is then placed in a hot-water oven kept at a temperature of 70° to 80° and allowed to remain there for 1 hour. It is then removed and allowed to cool for 1 hour longer. The condensation product, consisting of grey needles free from mineral matter, is then filtered off in a Gooch crucible containing a layer of asbestos; it is washed with cold water, and dried at 100° to 105° to constant weight (about 3 hours). The quantity of vanillin, x, is calculated from the weight of the product, y, by one of the following formulæ: $x = \frac{y + 15.7}{0.97}$ (for 50 c.c.), or $x = \frac{y + 38.25}{1.04}$ (for 100 c.c.). The presence of piperonal has very little effect on the estimation of vanillin by the above method.

A. Moulin (*Bull. Soc. chim.*, 1903, [iii], **29,** 278) has devised a color-imetric method for the estimation of vanillin in vanilla, based upon the conversion, by nitric acid, of the—$C_6H_3.OCH_3$ group in vanillin into methyl picrate.

The author claims that the method is very delicate, that the results agree with those given by the gravimetric methods, and that a difference of tint corresponding to 0.005 grm. of vanillin can be readily observed.

For the separation of *vanillin* and *coumarin*, as requisite in the analysis of mixed extracts of vanilla and Tonka beans, Hess and Prescott (*J. Amer. Chem. Soc.*, 1899, **21,** 256) recommend the following process: A weight of from 25 to 100 grm. of the extract is evaporated at 80°, water being added at intervals to keep the volume of the liquid constant until the alcohol has volatilised.   Lead acetate is then added with agitation as long as a precipitate forms, when the liquid is filtered through asbestos and the precipitate washed with a little hot water. The cooled filtrate is agitated with ether, and the ethereal layer sepa-rated and agitated with dilute ammonia in portions of 2 c.c.   This extracts the vanillin, whilst the coumarin remains dissolved in the ether, which is allowed to evaporate spontaneously.   The residual coumarin is purified by solution in light petroleum and finally weighed.   The m. p. (67°) and characteristic odour are sufficient for its identification. The vanillin may be recovered by slightly acidifying the ammoniacal solution with hydrochloric acid, extracting with ether, and evaporating cautiously.   After purification by solution in boiling light petroleum, the product should be pure vanillin, m. p. 80° to 81°.   After weighing, colour-tests may be applied for the identification of vanillin, bearing in mind that phenolic substances giving colourations with ferric salts are liable to be present.   Chloroform may be advantageously substituted for ether in the above process, which Hess and Prescott consider pref-erable to the alkali hydrogen sulphite method.

Winton and Silvermann (*J. Amer. Chem. Soc.*, 1902, **24,** 1128) recommend the above process, but use a 2% solution of ammonia in-stead of 10% as prescribed by Hess and Prescott, and they also prefer to weigh the vanillin and coumarin before dissolving in light petroleum. Any insoluble matter, which is usually insignificant in amount, may afterwards be weighed separately and allowed for if necessary.   6 ex-tracts prepared by Winton and Silvermann from different grades of vanilla pods by the formula of the United States Pharmacopœia (100 grm. of pods per litre of extract) had a sp. gr. ranging from 1.0104 to

1.0166, and contained vanillin, from 0.06 to 0.22% and cane-sugar, about 20%.

For details of the methods of analysis see *Connecticut Agric. Exp. Stat. Rep.*, 1901, **25**, 149 (*J. Soc. Chem. Ind.*, 1902, **21**, 1300) and *Bul.* 107, *Bureau of Chem., U. S. Dept. of Agric.* Winton and Bailey have further modified the process by diluting the sample to 3 times its volume and evaporating at 70° to the original bulk, and repeating this process in order to expel alcohol without losing vanillin. The coumarin after isolation is extracted with very light petroleum (b. p. 30 to 40°) which leaves undissolved any acetanilide present. The latter may be recognised by the usual tests (*J. Amer. Chem. Soc.*, 1905, **27**, 719).

Ritsert's tests, adopted by the United States Bureau of Chemistry, are as follows: One to three drops of a solution of chloride of lime (1:200) are added carefully to a portion of the extract in such a manner that the two liquids do not mix.   The formation of a beautiful blue colour at the junction of the two liquids indicates the presence of acetanilide.

(2) A small drop of potassium permanganate solution, when added to a second portion, gives a clear green colour if any appreciable amount of acetanilide is present.

(3)   A third portion is mixed with a small drop of a 3% solution of chromic acid.   Acetanilide gives a yellowish green solution changing to dark green after 5 minutes and forming a dark blue precipitate on addition of a drop of potassium hydroxide solution.

These tests are only conclusive when taken in conjunction with the m. p.

Essence of Vanilla.—Under this name, an alcoholic extract of vanilla beans is largely employed for flavouring purposes.   Much of the so-called "essence," however, is merely an alcoholic solution of artificial vanillin, coloured with caramel (sometimes with an admixture of artificial coumarin).   Genuine extract of vanilla pods contains a resin of dark red or brown colour, soluble in 50% alcohol, but precipitated on further dilution.   Hence when weaker spirit is used for preparing vanilla extract, potassium hydrogen carbonate or other alkali is used to effect solution of the resin, but the flavour of the preparation is prejudicially affected thereby.   Presence of resin, as indicated by precipitation on dilution with water, is more or less indicative of a genuine extract, whereas the presence of caramel and coal-tar dyes points to the vanillin being artificial.

The tests of the Bureau of Chem., U. S. Dept. of Agric., for the detection of these resins and caramel color are as follows:

Vanillin, although the most important, is not the only fragrant principle of the vanilla bean and true vanilla extract. The bean also contains, among the many extractive matters which enter into the food value and fragrance of the extract, certain resins which can be identified by a number of reactions. If the latter give negative results, it is evident that the extract was not made from vanilla beans.

Vanilla beans contain from 4 to 11% of these resins which vary from dark red to brown in colour and give rise to about one-half of the colour of the extract.

For the detection of the resins the extract is treated as follows: 50 c.c. of the sample to be examined are placed in a glass dish, and heated on a water-bath to expel the alcohol. When the latter has evaporated, the residue is diluted to the original volume with hot water. Provided alkali has not been used in the preparation of the extract, the resins will appear as a flocculent red or brown residue. The liquid is acidified with acetic acid to remove bases from the resins, the whole of which separate after a short time, leaving a partly decolourised, clear, supernatant liquid. The resin is collected on a filter and washed with water, the filtrate being reserved for further tests. When a portion of the filter with the attached resin is treated with a small quantity of dilute potassium hydroxide solution, the resin dissolves to a deep red solution which is precipitated by acids.

Unlike most resins, that derived from vanilla beans, when dissolved in alcohol, gives a solution of which the colour is very little changed by either hydrochloric acid or ferric chloride.

A portion of the filtrate from which the resin was separated, gives a precipitate with a solution of basic lead acetate, which is so bulky as almost to solidify. The filtrate from this precipitate is almost colourless.

Another portion of the filtrate from the resin may be tested for tannin with a solution of gelatin. Tannin occurs in the vanilla bean in varying but small quantities, a large proportion should not be found.

The presence of **caramel** as a colouring matter is indicated if, on shaking the bottle of vanilla extract, the bubbles formed are of a bright caramel colour, and retain this colour until all of them have disappeared. The colouring matter present in vanilla or tonka extracts is almost completely removed when the dealcoholised extract is

treated with basic lead acetate solution. If caramel is present, the filtrate and precipitate, if any, have the characteristic red-brown colour of this substance.

An imitation extract of vanilla made from Tonka beans is sometimes substituted in America for true vanilla extract. H. Leffmann distinguishes between the 2 by evaporating the extract on the water-bath, redissolving the residue in a little water, acidifying the solution slightly, and shaking with ether. The residue left on evaporating the ethereal layer is mixed with a very small amount of phloroglucinol and a drop of hydrochloric acid and the mixture heated on the water-bath. Vanillin gives a red colouration, but coumarin does not. This test would not serve for the detection of Tonka beans in admixture with vanilla.

The following method of detecting coumarin (*U. S. Dept. Agric. Bur. Chem. Bull.* 107) is given on the authority of Albert E. Leach ("Food Inspection and Analysis" p. 738). A few of the crystals are dissolved in a small quantity of hot water, the solution filtered if necessary, and the filtrate treated with a few drops of a N/10 solution of iodine in potassium iodide. In the presence of coumarin a brown precipitate will be formed, which on stirring or shaking collects in dark green flocks leaving a clear brown solution. The reaction is especially marked if the iodine reagent is applied with a glass rod to the solution to be tested on a white tile.

The following colorimetric method has been proposed by Moerk (*Amer. Jour. Pharm.*, 1891, **63,** 572) for the rough assay of essence of vanilla:

The vanilla extract is treated with freshly-precipitated lead hydroxide and to an aliquot part of the filtrate, after dilution, bromine water is added, drop by drop, until the colour of bromine no longer disappears on shaking the liquid. By careful addition of a 1% solution of ferrous sulphate a bluish-green colour is developed, which gradually increases in intensity to a maximum. By comparing this colour with that produced in a solution of known vanillin content, the estimation of the quantity of the vanillin in the extract may be effected.

iso-**Vanillin,** $C_6H_3(CHO)^1(OH)^3(OCH_3)^4$, is an isomeride of vanillin obtained by heating opianic acid under pressure with dilute hydrochloric acid, and is formed in small quantity, together with vanillin, in many reactions. It forms vitreous prisms, m. p. 115°, b. p.

179°, yielding a vapour which has an odour resembling that of vanilla and anise.   *iso*-Vanillin gives no colouration with ferric chloride.

Piperonal. $C_8H_6O_3$; *i. e.*,

Piperonal, or *heliotropin* as it is commercially named, has the constitution of *methylene-protocatechuic aldehyde.* It was originally produced by the gradual addition of a solution of potassium permanganate to one of potassium piperate obtained by the saponification of piperine, the alkaloid of pepper. The liquid acquires a pleasant odour like that of coumarin, and yields piperonal on distillation.

Piperonal is manufactured from *safrole*, $C_6H_3(C_3H_5)^1(O_2 . CH_2)^{3:4}$, a leading constituent of the oils of sassafras and camphor. By the action of sodium hydroxide the safrole is converted into *iso*safrole which is oxidised with potassium dichromate and sulphuric acid.

Piperonal crystallises in large lustrous prisms or thin plates, m. p. 37°. It has a very pleasant odour, closely resembling that of the heliotrope, and on this account is extensively employed in perfumery under the name of "heliotropin." Piperonal is very sparingly soluble in cold water, but more readily in hot, and dissolves very easily in alcohol and ether. It has the general characters of an aldehyde. Its compound with sodium hydrogen sulphite crystallises in laminæ and is but slightly soluble in water or alcohol. By treatment with oxidising agents or boiling with alcoholic potassium hydroxide piperonal is converted into *piperonylic acid* (page 513), whilst on reduction of its boiling aqueous solution by sodium amalgam it yields *piperonyl alcohol*, $C_6H_3 . (O_2:CH_2) . CH_2OH$, a sparingly soluble substance, m. p. 51°.

When heated under pressure at 200°, with dilute hydrochloric acid, piperonal is decomposed into protocatechuic aldehyde and finely divided carbon.

In doses of 0.5 to 1.0 grm. piperonal has been employed as an antiseptic and antipyretic of moderate power, but some observers find it to be devoid of physiological action. By far its most important application is in perfumery.

Piperonal is injuriously affected by exposure to a temperature above or approaching its m. p., and is preferably preserved in alcoholic solution. It is liable to the same kinds of adulteration as vanillin, and, in addition, to contain an admixture of vanillin itself.

GALLIC ACID AND ITS ALLIES.

By W. P. DREAPER, F. I. C.

Of the 6 possible compounds having the constitution of trihydroxy-benzoic acids, the 3 following isomers are well known:

Gallic acid	Pyrogallol-carboxylic acid	Phloroglucinol-carboxylic acid
C_6H_2 $\begin{cases} COOH(\text{1}) \\ OH(\text{3}) \\ OH(\text{4}) \\ OH(\text{5}) \end{cases}$	C_6H_2 $\begin{cases} COOH(\text{1}) \\ OH(\text{2}) \\ OH(\text{3}) \\ OH(\text{4}) \end{cases}$	C_6H_2 $\begin{cases} COOH(\text{1}) \\ OH(\text{2}) \\ OH(\text{4}) \\ OH(\text{5}) \end{cases}$

Of these compounds, gallic acid is the only one of practical interest.[1]

GALLIC ACID. $C_6H_2(OH)_3.COOH+H_2O.$

Gallic acid occurs naturally in the free condition in gall-nuts, tea, sumac, divi-divi, mangoes, pomegranates, and many other plants, and may be obtained artificially by fusing brom-hydroxybenzoic acid or bromo-protocatechuic acid with potassium hydroxide. It is usually prepared, however, by the action of boiling dilute sulphuric acid on ordinary tannic acid (tannin), or, as it is frequently termed, gallo-tannic acid.[2] In this change 1 molecule of tannic acid is hydrolysed,

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[1] PYROGALLOL-CARBOXYLIC ACID is obtained when pyrogallol is heated with potassium hydrogen carbonate (*Ber.*, 1885, **18**, 3205). It decomposes when heated to 195°, but may be sublimed without decomposition in a current of carbon dioxide. The solution gives a violet colouration with ferric chloride.

PHLOROGLUCINOL-CARBOXYLIC ACID is obtained by boiling phloroglucinol with an aqueous solution of potassium carbonate. It decomposes at 100° or when boiled with water into phloroglucinol and carbon dioxide.

[2] The tannin extract is introduced, in a crude state, into a lead-lined vacuum pan, together with the necessary quantity of sulphuric acid, and the whole is heated to about 50° to 65° in a vacuum of 500 mm. Nearly the whole of the gallotannic acid is converted into gallic acid, and the concentration is kept up by the reintroduction of spent mother-liquor from the crystallising pans. Under these conditions the brown amorphous products obtained when the operation is conducted in open vessels are no longer formed; and, after the reaction is complete, the liquor can be concentrated until the gallic acid begins to separate by crystallisation. The crude product is in the form of yellow crystals, which furnish a perfectly pure, colourless acid on double crystallisation in presence of animal charcoal free from lime.

taking up a molecule of water, with the formation of 2 molecules of gallic acid:

$$C_{14}H_{10}O_9 \quad + \quad H_2O \quad = \quad 2C_7H_6O_5.$$

Digallic or   Gallic acid.
tannic acid.
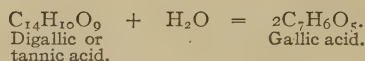
As in the case of many other changes of a hydrolytic nature, the same result may be brought about by the action of a natural ferment. The substance which most readily acts in this sense is the nitrogenised ferment contained in gall-nuts.[1] To bring about this change, the powdered galls are moistened with water and exposed to the air for several weeks. The dark-coloured mass is washed with a little cold water and then boiled with more water, which extracts the gallic acid.

Gallic acid occurs in the form of acicular prisms or silky needles, either white or, generally, of a faint buff colour, containing 1 molecule of water of crystallisation. It is odourless, and possesses a faintly acid taste. It loses its water of crystallisation at 100°. (Böttinger states that gallic acid does not become anhydrous below 120°, but this is apparently an error.)

When heated to a temperature of 210° to 220°, gallic acid melts and decomposes with formation of carbon dioxide and *pyrogallol*, $C_6H_6O_3$, which latter substance can be obtained as a sublimate. If the temperature be raised rapidly to 250°, water is given off in addition to carbon dioxide, and in the retort is found a considerable proportion of a deep-coloured, lustrous substance, which consists chiefly of *meta-gallic acid*, $C_6H_4O_2$.

Solvent	Parts of gallic acid dissolved	Solvent	Parts of gallic acid dissolved
Acetone................	29.4	Mixed benzene and ethyl acetate (1:1)............	0.77
Acetone + 5% water......	22.2	Ether (anhydrous)	2.5
Alcohol (absolute)	22.2	Ether (moist).............	2.7
Alcohol (90%)...........	18.9	Sodium chloride (26.9%) ..	0.96
Ethyl acetate...........	8.4	Water (at 12.5°)..........	0.76

[1] A. Fernbach (*Compt. rend.*, 1900, **131**, 1214) assumes that it is the mould-fungi formed in the gallic acid fermentation which bring about the hydrolysis of the tannin by a special ferment, *tannase*. Fernbach isolated this enzyme by cultivating *Aspergillus niger* in Raulin's liquid containing tannin in place of sugar. By precipitation with alcohol, H. Pottevin (*loc. cit.*) obtained tannase as a grey powder, the neutral or acidified solution of which is much more active than the original liquid. It acts most powerfully at 67°, is contained in sumac leaves, and appears to be widely distributed in the vegetable kingdom.

Gallic acid is soluble in about 100 parts of cold or 3 parts of boiling water. The hot solution deposits abundant crystals of the hydrated acid on cooling. Gallic acid is soluble in 5 parts of 90% alcohol, in 40 parts of ether, and in 12 of glycerol.[1] The figures for solubility of gallic acid according to the U. S. Pharmacopœia, at 25°, are: water 83.7 parts, alcohol 4.14 parts. It is only very slightly soluble in chloroform, benzene, and benzin.

An aqueous solution of gallic acid has an acid and astringent taste and readily undergoes decomposition. Gallic acid may be extracted from its aqueous solution by agitation with ether, or ethyl acetate.

Gallic acid is monobasic, and forms a series of well-defined, but unimportant, crystallisable metallic salts. The gallates of the alkali-metals are stable in the dry state or in acid solution, but in alkaline solution they readily absorb oxygen and become coloured, owing to the formation of *galloflavin*, a yellow dye of the xanthone series. Basic bismuth gallate is described on page 533.

Oxidising agents, such as arsenic acid and iodine, convert gallic acid into *ellagic acid*, which is probably a fluorene derivative.

According to Guignet (*Compt. rend.*, 1891, **113,** 200), when a warm solution of gallic acid is added to a warm mixture of zinc powder and ammonia, it is completely converted into benzoic acid after being heated to 60° for some hours. Benzoic acid is also formed when gallic acid is heated with zinc and dilute sulphuric acid, but in this case the benzoic acid remains undissolved.

When gallic acid is heated with 5 times its weight of strong sulphuric acid to 100°, it is converted into *rufigallic acid*, $C_{14}H_8O_8$. The liquid first becomes red and next purple, and if then poured into water, nearly pure rufigallic acid is precipitated.[2] If, in the above process, a portion of the gallic acid be replaced by benzoic acid, the product is *anthragallol*, one of the isomeric trihydroxy-anthraquinones.

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[1] The table (page 526), based on the observations of Rosenheim and Schidrowitz (*Trans.*, 1898, **73,** 882) shows the solubility of gallic acid in 100 parts of various solvents at 15°.

[2] RUFIGALLIC ACID, OR RUFIGALLOL, is a *hexahydroxyanthraquinone* of the constitution: $C_{14}H_2O_2(OH)^1(OH)^2(OH)^3(OH)^5(OH)^6(OH)^7$. It forms small, shining, reddish-brown crystals containing $2H_2O$, but becomes anhydrous at 220°, and sublimes at a higher temperature in cinnabar-red prisms. Rufigallic acid dissolves sparingly in hot water, alcohol, and ether. It dissolves with an indigo-blue colour in alkali hydroxide, and gives an indigo-blue precipitate with baryta water. When heated with zinc dust it is reduced to anthracene, $C_{14}H_{16}$.

When pyrogallol is fused with ammonium oxalate it yields ammonium rufigallate, which dissolves in water with red colour, and gives the following reactions: Potassium ferricyanide and potassium bichromate give a dark brown precipitate insoluble in alcohol. Ferric chloride gives no black colouration, and neither sodium nitroprusside nor platinic chloride produce either precipitate or change of colour. On adding a few drops of acetic acid, and then potassium cyanide and mercurous nitrate, a black precipitate is obtained. Alkali hydroxide cause a change to brown but not to black.

Gallic acid is absorbed by certain organic tissues, such as hide and silk, in the same manner as tannic acid, but far less readily and completely. Vignon (*Compt. rend.*, 1895, **121,** 916) states that ungummed silk absorbs from 7 to 8% of its weight from a 4% solution of gallic acid at a temperature of 80°; but with a bath of 1% strength the absorption is practically *nil*. From a mixed bath of tannic and gallic acids the former is preferentially absorbed.

Gallic acid and its derivatives are used to a considerable extent in medicine. Gallic acid is also used as a reducing agent in photography and is a constituent of certain hair-dyes. It finds employment in the manufacture of pyrogallol.

Analytical Reactions of Gallic Acid.—An aqueous solution of gallic acid gives the following indications:

On the addition of a solution of ferric chloride a deep blue precipitate is formed, which is soluble in excess of the reagent with green colour. The exact colour of the precipitate is affected by the concentration of the solutions. An excess of gallic acid destroys the colour, and reduces the iron to the ferrous state. A similar change occurs on boiling the liquid.

In the absence of air, a solution of ferrous sulphate gives a white precipitate with a concentrated solution of gallic acid. With a dilute solution no immediate change occurs, but on exposure to air the liquid becomes bright blue, and deposits a black precipitate without becoming decolourised.

W. H. Ince (*Pharm. J.*, 1887, [3], **17,** 461) prepares a neutral solution of ferrous chloride by decomposing cupric chloride by iron filings or wire. He adds this reagent to the solution to be tested for gallic acid, and then gradually adds bromine in excess. Under these conditions, gallic acid gives a faint blue colour on first adding the ferrous chloride, and this is changed to indigo-blue on cautious addition of bromine water or vapour, but the liquid is decolourised on adding excess. Gallotannic acid gives a red tint changing to green with excess.

On addition of excess of alkali hydroxide to a solution of gallic acid the liquid turns yellow, and ultimately brown and black on exposure to the air, from formation of tanno-melanic acid. The change is accelerated by boiling. On neutralising the black liquid with acetic acid and adding lead acetate, a black precipitate is thrown down. If sodium hydrogen carbonate be used instead of alkali hydroxide,

the liquid becomes indigo-blue and deposits a deep bluish-green precipitate, which is turned red by acids.

Lime-water in excess produces a white precipitate with solutions of gallic acid, changing very rapidly to blue.

When ammonium chloride and ammonia are added to a solution of gallic acid no precipitate is formed, but a strong red colour is developed if the solution is strong, or a greenish-coloured ring at the junction of the layers of the liquids is formed if the solution be weak.

A red colour is produced in solutions of gallic acid by chlorine water and ammonia.

With a solution of potassium antimony tartrate, gallic acid yields a white precipitate even in very dilute solutions, and the filtrate is practically free from gallic acid. The action is prevented by ammonium chloride, or acetate. Precipitation as gallate has been proposed as a means of estimating antimony.[1]

Gallic acid reduces Fehling's solution only slowly and imperfectly, with formation of acetic and pyrotartaric acids and other products (C. Böttinger, *J. Soc. Chem. Ind.*, 1891, **10**, 480). Gallic acid reduces gold and silver solutions (rapidly when hot), and decolourises an acid solution of potassium permanganate, being oxidised to hydro-rufigallic acid, $C_{14}H_8O_5$.

In the absence of other reducing agents, gallic acid may be estimated by titration in an acid solution with permanganate, preferably in presence of indigo. If tannic acid be present, it must first be separated by precipitation.

Gelatin or "collin" cannot be used for this purpose owing to the large percentage of gallic acid carried down by the tannic acid coagulum (Dreaper, *Chem. News*, 1904, **90**, 111).

No precipitate (distinction from tannic acids) is produced with gallic acid by dilute solutions of alkaloids, gelatin, albumin, or starch, but a mixture of gum-arabic and gelatin is precipitated.

In very concentrated solutions gallic acid is precipitated by albumin (Dreaper. and Wilson, *J. Soc. Chem. Ind.*, 1906, **25**, 515).

According to Griggi, a 3% solution of potassium cyanide produces, with a 1% solution of gallic acid, a fine ruby-red colouration, which shortly disappears, but can be restored by agitating the liquid. Tannic acid and pyrogallol give a yellowish-red colour when similarly treated.

[1] The British Pharmacopœia (1898) erroneously states that gallic acid is not precipitated by antimony tartrate.

If hydrogen peroxide be added in addition to potassium cyanide, gallic acid still gives a ruby-red colouration; but with tannic acid the colour is yellowish-brown, and with pyrogallol a dirty white turbidity is produced.

The following table exhibits the reactions of gallic acid in juxtaposition with those of gallotannic and pyrogallic acids, to which substances gallic acid presents many points of resemblance:

Reagent	1% Solution of:		
	Gallotannic acid	Gallic acid	Pyrogallol
1. Gelatin........	White or buff coloured precipitate.	No change, except in presence of gum-arabic.	No change.
2. Ferrous sulphate (free from ferric salt).	No change; white in concentrated solution, darkening on exposure.	No change; white in concentrated solution, darkening on exposure.	White precipitate, changed to blue solution by least trace of ferric salt.
3. Ferric chloride.	Blue-black ppt.; colour destroyed by boiling.	Deep blue colouration, destroyed by boiling.	Red colour, turning brown on heating.
4. Ferric acetate.	Blue-black ppt.	Purple-black ppt.	Purple-black colour.
5. Ammoniacal ferricyanide.	Deep red colouration destroyed by moderate excess of the reagent.	Vermilion-red colouration, only destroyed by a large excess of reagent.	Intense brown colour.
6. Ammoniacal picric acid.	Reddish.	Red colouration, rapidly changing to fine green.	Reddish colour.
7. Lime-water in excess; or barium chloride and ammonia.	White precipitate, rapidly becoming blue.	White precipitate, very rapidly becoming blue.	No ppt.; immediate purple colour becoming brown in the air.
8. Lead acetate..	White ppt. insoluble in actic acid.	White ppt., soluble in acetic acid.	Slight precipitate.
9. Lead nitrate..	White precipitate.	No change.	No change.
10. Tartar emetic.	White ppt. insoluble in ammonium chloride.	White ppt. soluble in ammonium chloride	No change.
11. Bismuth nitrate	White precipitate.	Pale yellow ppt.	Dark greenish ppt.
12. Ammoniacal cupric sulphate.	Precipitate.	No precipitate.	Deep purple-brown colouration.
13. Potassium cyanide.	Yellowish-red.	Ruby-red colour, disappearing on standing, but restored by shaking with air.	Yellowish-red.

With Hübl's iodine solution, gallic acid yields a golden-yellow substance which is readily soluble in water. Tannic acid absorbs less iodine than gallic acid, and gives a yellow, granular product which is nearly insoluble in water.

An ammoniacal solution of potassium ferricyanide produces with gallic acid a very bright red colouration, destroyed only on adding a large excess of the reagent.

An aqueous solution of picric acid to which an excess of ammonia has been previously added produces with gallic acid a red colouration, changing in a few seconds to a beautiful green.

Gallic acid gives a somewhat similar and delicate reaction on addition of a faintly alkaline solution of sodium arsenate, when the surface of the liquid exposed to the air rapidly becomes deep green.

When gallic acid mixed with twice its weight of phenylhydrazine is heated to 100° or a slightly higher temperature and then boiled with water, or when the aqueous solutions of the two substances are mixed and boiled, a compound is obtained which dissolves in very dilute sodium hydroxide solution with reddish-yellow, orange, or golden colouration. Tannin, on similar treatment, yields a splendid greenish-blue solution, gradually turning yellow.

Pure gallic acid is optically inactive, while gallotannic acid is active (Rosenheim and Schidrowitz, *Trans.*, 1898, **73**, 880).

W. P. Dreaper (*J. Soc. Chem. Ind.*, 1893, **12**, 412, *and Chem. News*, 1904, **90**, 111) has devised a process by which gallic acid can be estimated volumetrically with very fair accuracy. It consists in heating the solution to be tested to about 90° after adding about 1 grm. of precipitated calcium carbonate and subsequently cooling to about 25°. In this way the calcium salt of gallic (or tannic) acid is formed before titration. A solution of copper sulphate containing 15 grm. per litre is then added, with agitation, until the precipitate shows a tendency to collect at the bottom of the liquid. A drop of the supernatant liquid is then removed and pressed on a doubled, square inch of filter-paper, to the under leaf of which a drop of solution of potassium ferrocyanide is then applied. If the action is complete, a faint pink colouration will be observed, owing to the formation of cupric ferrocyanide. If no colour is obtained, more copper sulphate must be cautiously added and the testing of a drop of the liquid repeated. Dreaper found 0.5 grm. of the purest gallic acid obtainable to require 45 c.c. of the standard copper solution for its precipitation.[1]

Gallotannic acid behaves in the above process exactly like gallic acid, except that 0.5 grm. of the purest specimen obtainable requires a

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[1] A slight correction should be made for the excess of copper solution requisite to yield a visible reaction, as ascertained by a blank experiment.

different amount of the copper solution for its precipitation. Hence when a mixture of tannic and gallic acids is to be analysed, it is necessary first to separate the former. This is effected by Dreaper by adding to 50 c.c. of the original solution 5 grm. of barium sulphate, followed by 10 c.c. of a solution containing 20 grm. of lead acetate and 60 c.c. glacial acetic acid to the litre, which should be added gradually with constant shaking. The liquid is then filtered through a dry filter-paper, and a small quantity of anhydrous sodium sulphate (o. 5 grm.) added. After 5 minutes the lead sulphate is filtered off through another filter-paper and the resulting solution titrated with copper sulphate solution after ascertaining its volume and heating with calcium carbonate. In all three operations the calcium carbonate used must be pure. The quality "precipitated for analysis" is the best. By this treatment the tannic acid is completely removed, and the gallic acid can be estimated by titrating 40 c.c. of the filtered liquid with copper solution in the manner already described.

An approximate estimation of the gallic acid may be made by titrating the filtrate with standard permanganate in presence of sulphuric acid and indigo-carmine.

Another method of separating gallic acid from tannins depends on the insolubility of cupric gallate in water, and its solubility in ammoniacal liquids. The solution is precipitated by excess of cupric acetate, the precipitate washed and digested with a cold solution of ammonium carbonate. The solution, filtered from any insoluble tannate of copper, is evaporated to dryness, the residue moistened with nitric acid, ignited, and the resultant cupric oxide weighed. Its weight, multiplied by 0.9, gives the weight of gallic acid. This method is sometimes applicable to the separation of gallic acid from gallotannic and quercitannic acids, but the copper salts of some varieties of tannin are soluble in ammonium carbonate.

In the absence of tannic acid and other substances which interfere with the action, gallic acid may be estimated by digesting the solution containing it with a known weight of recently ignited oxide of zinc. The insoluble zinc powder is filtered off and washed, dried at 110°, and finally weighed. The increase in weight may be regarded as the amount of gallic acid taken up. Gallic acid may be separated from many varieties of tannin by agitating it in aqueous solution with ether.

The ordinary hide powder process as used in the estimation of tannins is quite useless in the case of gallic acid, as will be seen from

figures given by Dreaper (*Chem. News*, 1904, **90,** 111) where results showing errors amounting to between 27.0 and 45.6 % are given.

Esters and Derivatives of Gallic Acid.

A number of derivatives of gallic acid have recently found application in medicine. The following are the most important of these:

Bismuth Subgallate, brought out under the trade name of "dermatol" is a basic gallate of bismuth of the formula, C_6H_2-$(OH)_3.COOBi(OH)_2$. It forms a soft, bright yellow, tasteless, odourless powder, which reddens litmus-paper, but is almost insoluble in water, alcohol, and ether. It should be wholly soluble in dilute acids and in sodium hydroxide solution, and should give no indication for nitrates with diphenylamine. Bismuth subgallate is a valuable substitute for iodoform, and in doses of 0.25 to 0.5 grm. is employed internally in the treatment of diarrhœa.

The following tests are given in the United States Pharmacopœia.

Bismuth subgallate should yield not less than 52% nor more than 57% of pure bismuth oxide.

An amorphous, bright yellow powder, somewhat variable in chemical composition, without odour or taste, and permanent in the air.

Insoluble in water, alcohol, and ether; readily, with decomposition, in hydrochloric, nitric, and sulphuric acids if these be heated; insoluble in very dilute mineral acids; readily soluble in solutions of the alkali hydroxides, forming a clear yellow-coloured solution, which readily changes to a deep red.

When heated to 120° the salt loses from 5 to 7% of water, and on subsequent heating to redness it at first chars, finally leaving a yellow residue, which is soluble in hydrochloric and nitric acids and is blackened by ammonium sulphide T. S.

Upon thoroughly agitating 0.1 grm. of bismuth subgallate with an excess of hydrogen sulphide T. S., a black precipitate results; on filtering and then boiling the filtrate to remove the dissolved gas the cold filtrate, after the addition of 1 drop of ferric chloride T. S., will assume a blue-black colouration.

If 9.5 grm. of the salt be well shaken with 5 c.c. of alcohol and filtered at once, the filtrate should not turn moistened blue litmus-paper red (absence of free gallic acid).

If o. 5 grm. of bismuth subgallate be well mixed with 5 c.c. of dilute sulphuric acid and 5 c.c. of ferrous sulphide T. S., the mixture filtered and the filtrate cautiously poured, without shaking, over 5 c.c. of sulphuric acid (free from nitrous compounds) contained in a test-tube, no brown ring should form after standing for ten minutes (limit of nitrate).

If 3 grm. of bismuth subgallate be ignited in a porcelain crucible, and, after cooling, nitric acid be cautiously added to the residue drop by drop, warming until it is dissolved, then evaporating to dryness and again igniting and cooling, should, after concentrating to about 4 c.c., be poured into 100 c.c. of water, and after filtering and evaporating the filtrate on a water-bath to 30 c.c., again filtering, and dividing this filtrate into portions of 5 c.c., then each of these should respond to the test for purity described under bismuth subcarbonas.

The residue resulting from the ignition and subsequent treatment of 2 grm. of the salt, as described below, should not respond to Bettendorf's test for arsenic.

If 1 grm. of bismuth subgallate be thoroughly ignited in a porcelain crucible, and, after cooling, 5 c.c. of nitric acid be added to the residue, drop by drop, warming until complete solution has been effected, this, upon evaporating to dryness and again igniting, should leave a residue of bismuth oxide weighing not less than o. 52 grm. nor more than o. 57 grm.

Average dose, o. 250 grm. = 250 milligrammes (4 grains).

"**Airol,**" a compound of the formula $C_6H_2(OH)_3.COOBi(OH)I$, possesses at once the absorbent properties of dermatol and the antiseptic properties of its iodine. It forms a greenish-grey, odourless, tasteless powder, which loses iodine on exposure to moist air. "*Iodogallicin*" is a methyl-derivative of airol.

"**Gallicin,**" or **methyl gallate,** $C_6H_2(OH)_3.COO(CH_3)$, is prepared by passing a current of dry hydrochloric acid gas through a solution of gallic acid in methyl alcohol. It forms fine needles or prisms which melt at 202°, and are readily soluble in water and alcohol. It is used as an antiseptic dusting powder and in certain eye diseases.

"**Bismal.**"—Gallic acid readily condenses with formaldehyde to form substances typified by *methylene-digallic acid*, or *methylene gallate*, $C_6H_2(OH)_3.CO.O.CH_2.OCO.(OH)_3C_6H_2$. The *bismuth* salt of

this body, said by Merck to be $4C_{15}H_{12}O_{10}+3Bi(OH)_3$, is the "bismal" of commerce. It forms a bluish-grey, voluminous powder, soluble with yellow or red colour in alkalies and reprecipitated by acids. It is recommended in doses of 0.1 to 0.3 grm. as an internal astringent in chronic diarrhœa (compare *Ber.*, 1898, **31**, 259).

"Gallobromol" is a *dibromogallic acid*, $C_6Br_2(OH)_3.COOH$. It is obtained by the direct action of bromine on gallic acid, and forms fine white needles of bitter taste, almost insoluble in cold, but readily soluble in boiling water. It is also dissolved by alcohol and ether. It is a valuable substitute for metallic bromides as a sedative in nervous complaints.

"Gallanol," or *galanilide*, $C_6H_2(OH)_3.CO.NH.C_6H_5$. This substance forms white crystals melting at 205°, soluble in water, alcohol, and ether. It has marked astringent properties and, being less irritant and non-poisonous, is preferred to chrysophanic acid and pyrogallol in the treatment of skin diseases.

Gallacetophenone, $C_6H_2(OH)_3.CO(CH_3)$, has already been described on page 428.

Pyrogallol. Pyrogallic Acid. $C_6H_6O_3; i.e., C_6H_3 \begin{cases} OH^{(1)} \\ OH^{(2)} \\ OH^{(3)} \end{cases}$

Pyrogallol has the constitution of a trihydroxy-benzene, and hence is isomeric with phloroglucinol and hydroxy-quinol. Thus:

	Pyrogallol	Phloroglucinol	Hydroxyquinol
Position of OH-groups in benzene-ring.	1 : 2 : 3	1 : 3 : 5	1 : 2 : 4
M. p.,°	131°	218°	140.5°
Colouration with ferric chloride...	Red	Dark violet	Greenish-brown.

Phloroglucinol is described in Vol. 5. Hydroxyquinol has no practical interest.

Pyrogallol is produced when carbon dioxide is split off from gallic acid or from the isomeric pyrogallol-carboxylic acid, in both of which bodies the 3 hydroxyl groups occupy consecutive positions in the benzene nucleus. Pyrogallol is formed when the above-named acids

are heated alone, as was first observed by Scheele (1786), but better by heating with water to 210°. It may also be prepared by heating a solution of commercial gallotannic acid in glycerin to 200°, diluting with water, and extracting the pyrogallol by agitation with ether.

Pyrogallol may be conveniently obtained by mixing gallic acid with twice its weight of aniline. The mixture at first becomes liquid, and then suddenly solidifies with rise of temperature. On heating the product to 120° till carbon dioxide is no longer evolved, *aniline pyrogallate* separates out on cooling in long needles, melting at 55° to 56°. On treating this compound with cold benzene, pure aniline is dissolved, and pyrogallol remains insoluble. Several organic bases besides aniline effect the same result, but pyridine does not react until heated considerably above its b. p.

Pyrogallol can also be prepared by fusing either of the two parachlorphenol-disulphonic acids with potassium hydroxide, and it results from the action of fused alkali hydroxide on hæmatoxylin.

Pyrogallol forms white leaflets or thin lustrous needles, having a sp. gr. of 1.463. It melts at 131° to 132° (not at 115° to 118°, as sometimes stated). When cautiously heated above this temperature, pyrogallol can be sublimed without decomposition; but when rapidly heated to 250°, it loses the elements of water and is converted into a more or less indefinite substance termed *metagallic acid*, which forms a black, amorphous mass insoluble in water but soluble in alkalies.

Pyrogallol dissolves in less than 3 parts of cold water, to form a solution of acid and bitter taste. It is also freely soluble in alcohol and ether, but practically insoluble in absolute chloroform.

Pyrogallol forms salts with bases, but its acidic characters are not very strongly marked, and the salts are very unstable.[1] Pyrogallic acid itself is stable in the dry state, when the atmosphere is free from ammonia, but in moist or ammoniacal air it gradually darkens and turns brown. In aqueous solution this change occurs far more rapidly, and is attended with absorption of oxygen.[2] In the presence of am-

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[1] *Barium pyrogallate.* $C_6H_3(OH)O_2Ba + 4H_2O$, has been prepared by mixing aqueous pyrogallol with excess of baryta water. It forms colourless needles which rapidly blacken in the air, and are decomposed when boiled with water.

[2] The oxidation of pyrogallol in acid or neutral solutions results in the formation of purpurogallol or purpurogallin, a body of the formula $C_{20}H_{16}O_9$. It is most readily obtained by treating a solution of 20 parts of pyrogallol in 330 parts of water with a solution of 87 parts of potassium ferricyanide in 330 parts of water. Gas is evolved, the solution loses its deep red colour, and purpurogallin separates, the oxidation being complete in about half an hour. Purpurogallin crystallises from alcohol in brown velvet-like needles, melting at

monia or fixed alkali, the absorption of oxygen by pyrogallol is extremely rapid, the liquid quickly becoming brown and finally black. This behaviour of an alkaline solution of pyrogallol is employed for the estimation of oxygen in air and other gaseous mixtures, but has been objected to on the ground that the absorption of oxygen is attended with simultaneous evolution of carbonic oxide.[1]

According to M. Berthelot (*Compt. rend.*, 1898, **126,** 1459), the chief products of the oxidation of pyrogallol in presence of potassium or sodium hydroxide are carbon dioxide and about 86% of a dark brown substance soluble in water having the composition $C_{20}H_{20}O_{16}$. A dark red, crystallisable substance, containing $C_{20}H_{20}O_{11}$, soluble in ether and having some of the properties of purpurogallin (from which it differs by $2H_2O$), is formed in the early stages of oxidation; while another substance soluble in ether, and of the probable formula $C_{16}H_{16}O_{12}$, exists in the final products in quantity equal to about 10% of the original pyrogallol.

With lime-water, or calcium chloride and ammonia, in presence of air, pyrogallol gives a fine purple colouration, rapidly changing to brown, but no precipitate is produced. The test is delicate and characteristic.[2]

Pyrogallol rapidly reduces salts of mercury, silver, and gold, with

156°, and volatilising at 200° with partial decomposition. It dissolves with difficulty in water, but readily in alcohol and ether, and is soluble in alkalies to form unstable blue compounds. The sodium salt contains Na_4, and gives with barium chloride an almost insoluble precipitate of the barium compound. In strong sulphuric acid, purpurogallin dissolves to a liquid which gives an intense violet colouration when a trace of nitrous acid or a nitrite is added. The colour is fugitive, but the test is said to be delicate and characteristic (S. C. Hooker, *Ber.*, 1887, **20,** 3259).

[1] F. Clowes (*Proc. Chem. Soc.*, 1895, p. 200) finds that when the absorption of oxygen is effected by a solution containing 10 grm. of pyrogallol and 24 of potassium hydroxide per 100 c.c., no carbon monoxide is evolved unless the oxygen in the gaseous mixture exceeds 28%, and in such cases perfectly accurate determinations of oxygen are obtainable if the carbon monoxide evolved be absorbed by cuprous chloride before taking the reading. If the proportion of alkaline hydroxide be increased to 120 grm. per 100 c.c., no evolution of carbonic oxide occurs. The question has been further studied by M. P. E. Berthelot (*Compt. rend.*, 1898, **126,** 1066, 1459), who states that in presence of 3 molecules of potassium or sodium hydroxide 1 molecule of pyrogallol absorbs 3 atoms of oxygen, the carbon monoxide evolved being 2.2% of the volume of oxygen absorbed. With 3 equivalents of barium hydroxide, however, only 1 atom of oxygen is absorbed, and less carbon monoxide is formed. With ammonia the absorption is at first very rapid, but is ultimately very slow, 4 atoms of oxygen being ultimately absorbed. No nitrates are formed, but possibly an azo-compound is produced.

[2] For examining the behaviour of pyrogallol with lime-water, it is convenient to employ a nitrometer filled with mercury. A few cubic centimetres of the solution to be tested for pyrogallol are first allowed to enter through the tap, and the cup is rinsed with water, which is allowed to enter in its turn. Ammonia is next run in, when a slight brown colouration is usually produced owing to dissolved oxygen. On now allowing lime-water or calcium chloride to enter, a fine but rapidly fading purple colour will be developed, and this will be greatly intensified on admitting air and agitating the tube; in fact, in the entire absence of oxygen, the purple-blue colour would probably not be produced. In the absence of calcium (or barium) compounds only a brown colour is produced on admitting air. Addition of potassium ferricyanide to the ammoniacal liquid produces an immediate dark brown colouration, apparently owing to the formation of the same oxidation-product as is produced by admitting air; but ferricyanide prevents the formation of the blue colour with calcium salts, probably by immediately forming the more highly oxidised brown product.

precipitation of the metal and formation of acetic and carbonic acids. Fehling's solution and potassium ferricyanide are also reduced, and potassium permanganate in acid solution is rapidly decolourised with evolution of carbon dioxide.

With ferrous sulphate, especially if a little ferric salt be present, pyrogallol gives a blue colouration, rapidly changing to green and red; and with ferric chloride it at once gives a red colouration, turning brown on heating the liquid.

The aqueous solution of pyrogallol is turned brown by nitrous acid. The test is very delicate.

Pyrogallol does not precipitate a solution of gelatin.

Pyrogallol might probably be estimated by titration in acid solution with standard permanganate, or perhaps by means of Fehling's solution.

Pyrogallol condenses with formaldehyde to form a product of a deep red colour. Pyrogallol forms several well-defined sulphonic acids, which give crystallisable salts (M. Delage, *Compt. rend.*, 1900, **131**, 450).

When fused with ammonium oxalate, pyrogallol yields *ammonium rufigallate.*

Pyrogallol possesses well-marked toxic properties, and a case of fatal poisoning by its ingestion is on record (*Pharm. Jour.*, 1896, **2,** 260). The lethal dose is about 0.1 grm. per kilo-grm. of body-weight and the symptoms are similar to those produced by phosphorus-poison-ing. Pyrogallol retards the heart's action and alters the appearance of the blood (Gibbs and Hare, *Amer. Chem. Jour.*, 1890, **12,** 365).

Ethers and Esters of Pyrogallol.

Some of the pyrogallyl esters are prepared on a small scale for medicinal purposes.

Pyrogallyl monacetate, $(OH)_2(O.C_2H_3O_2)$, is known under the name of "*Eugallol.*" It is very soluble in water, but is of too irritating a nature to be used in ordinary dermatological practice. It is of a syrupy consistence and easily soluble in acetone. When a very energetic action on a limited portion of the skin is required, this body has been found very useful, as it can easily be applied as a solution in acetone, which rapidly evaporates and leaves the eugallol on the

desired place. The commercial "Eugallol" contains 33% of acetone. *Pyrogallol triacetate* is a white powder insoluble in water, and is known as *"Lenigallol."* It has been very successfully employed in cases of psoriasis. The *disalicylate* is known as "saligallol," and is sometimes employed in similar cases (see page 499).

Pyrogallol dimethyl ether, $C_6H_3(OH).(OCH_3)_2$, and its homologues occur in the less volatile fractions of beechwood-tar. They owe their chief interest to the remarkable series of colouring matters originally prepared from them by Runge.

By condensing pyrogallol-dimethyl ether with tiglic aldehyde, Doebner has obtained an artificial resin closely resembling the natural products. When guaiacol is condensed in conjunction with dimethyl gallate, the resin obtained is isomeric with *guaiaconic acid,* one of the constituents of guaiacum-resin, Doebner's results support the view that the natural resins are in many cases condensation products of phenols with aldehydes

PHTHALIC ACID AND THE PHTHALEINS.

By W. A. DAVIS, B. Sc., A. C. G. I.

PHTHALIC ACIDS.

Benzenedicarboxylic Acids, $C_6H_4(CO_2H)_2$.

Three isomeric acids of the above composition are known, differing from each other in their properties and structure, according to the relative positions of the carboxyl groups in the benzene nucleus. Thus, on oxidation with dilute nitric acid or an alkaline solution of potassium permanganate, the 3 isomeric xylenes yield the corresponding phthalic acids. These may, in fact, be regarded as the final products of the limited oxidation of the great majority of benzene derivatives containing 2 side-chains. Hence the differentiation of the phthalic acids affords, in this as in many other cases, a valuable means of distinguishing between allied or isomeric compounds of the aromatic series, and of studying their constitution. The formation of phthalic acid, for example, by the oxidation of naphthalene affords most valuable evidence of the constitution of that hydrocarbon.

The following table exhibits the leading points of difference between the isomeric phthalic acids:

	Orthophthalic or ordinary phthalic acid	Metaphthalic or isophthalic acid	Paraphthalic or terephthalic acid
Formula..............	$C_6H_4 \begin{cases} (1)\ CO.OH \\ (2)\ CO.OH \end{cases}$	$C_6H_4 \begin{cases} (1)\ CO.OH \\ (3)\ CO.OH \end{cases}$	$C_6H_4 \begin{cases} (1)\ CO.OH \\ (4)\ CO.OH \end{cases}$
Chief sources and modes of formation.	Oxidation of ortho-xylene, alizarin, purpurin, benzene, naphthalene, and naphthalene tetrachloride.	Oxidation of meta-xylene and colophony.	Oxidation of para-xylene, p-toluidine, turpentine oil, cymene, cumin oil, eucalyptus oil, etc.
Crystalline form.......	Monoclinic prisms or nacreous laminæ.	Slender hair-like needles.	Amorphous or crystalline powder.

	Orthophthalic or ordinary phthalic acid	Metaphthalic or isophthalic acid	Paraphthalic or terephthalic acid
M. p................	213° when rapidly heated, giving the anhydride.	Above 300°.	Sublimes without melting.
Solubility in water......	Cold, 1 in 180 parts; boiling, more easily soluble (1 : 6).	Cold, 1 in 7,800; boiling, 1 in 460 parts.	Cold, very slight; boiling, sparingly.
Solubility in alcohol...	1 in 10 parts.	Readily.	Very slight.
Solubility in ether.....	1 in 146 at 15°.	....	Insoluble.
Action of chromic acid mixture.	Completely oxidised to water and CO_2.	Not affected.	Not affected.
Barium salt..........	Small scales or silky needles, only slightly soluble in hot water.	Crystallises in readily soluble needles, containing $6H_2O$.	White granular powder or concentrically arranged tablets containing $4H_2O$, soluble in 350 parts of cold water.
Silver salt..........	Crystalline and moderately soluble; detonates when rapidly heated.	Amorphous precipitate; forms Pharaoh's serpents on heating.	Amorphous precipitate, blackening in the light.
Dimethylester, $C_6H_4(CO_2Me)_2$.	Liquid, b. p. 282°.	Solid, m. p. 64°.	Solid, m. p. 140°.

ORTHO-PHTHALIC ACID,

CO.OH

CO.OH

Ordinary phthalic acid was formerly manufactured on the large scale mainly by converting naphthalene into the tetrachloride, and heating this with 5 to 6 parts of nitric acid of sp. gr. 1.36, till entirely dissolved, when the excess of nitric acid was expelled, and the phthalic acid crystallised out on cooling. It may be purified by re-crystallisation from hot water. The yield by this process is about 30% of the naphthalene used. Phthalic acid may also be obtained by treating naphthalene direct with nitric acid of 1.15 sp. gr., but only about 40% of the theoretical yield is obtained.

According to H. Luddens (*J. Soc. Chem. Ind.*, 1891, **10,** 758), the greater part of the phthalic acid employed in the manufacture of eosin and other phthalein dyes is prepared by the direct oxidation of naphthalene by chromic acid mixture (*sodium* dichromate and sulphuric acid), notwithstanding the general impression that phthalic acid is destroyed by this reagent. This has, however, now been largely superseded by the Badische Anilin- und-Sodafabrik process by which phthalic acid used in the production of synthetic indigo, is manufactured. This consists in heating naphthalene with fuming sulphuric acid at a temperature of 300° in presence of mercury sulphate,

mercury, or its oxides, which act catalytically (English Patent, 18 221, 1896).

According to Lossen, the m. p. of phthalic acid is 184°, while Ador states that the crystals melt at 213° and the powder at 203°. These different results depend on the rapidity with which the acid is heated, as a small quantity of the anhydride is formed which lowers the m. p. of the rest of the material. Gräbe (*Ber.*, 1896, **29,** 2806) gives the m. p. as about 195°. Neither iso- nor tere-phthalic acid forms an anhydride.

Phthalic acid is readily extracted from aqueous liquids by agitation with ether or benzene, but is insoluble in chloroform (distinction from benzoic acid).

When heated to 330° with a single equivalent of lime, phthalic acid yields calcium benzoate and carbonate: $2C_8H_6O_4 + 2CaO = Ca(C_7H_5O_2)_2 + CaCO_3 + H_2O$. When heated with a larger proportion of lime or other strong base, phthalic acid yields a carbonate and benzene: $C_8H_6O_4 + 2CaO = 2CaCO_3 + C_6H_6$.

By treatment with fuming nitric acid, phthalic acid is converted into nitrophthalic acid, $C_8H_5(NO_2)O_4$, but by strong chromic acid mixture it is completely oxidised.

By treatment with zinc and acetic acid, phthalic acid is converted into phthalide, $C_6H_4{<}^{CH_2}_{CO}{>}O$, diphthalyl, $C_{16}H_8O_4$, being also formed.

When reduced with sodium amalgam phthalic acid gives different *hydrophthalic acids* according to the conditions employed. These reduced acids are of considerable stereochemical interest (see Baeyer's researches, *Annalen*, Vols. **245, 251, 258, 266, 269**).

When distilled with aniline, phthalic acid is converted into phenyl-phthalimide or *phthalanil*, $C_6H_4{<}^{CO}_{CO}{>}N\,Ph$, a substance which crystallises from alcohol in needles melting at 205°, but volatile at a lower temperature. Phthalanil has been recommended as a febrifuge.

Besides the extensive employment of its anhydride in the production of dyes, phthalic acid itself has found valuable application as a means of separating certain of the alcoholic constituents of essential oils in a state of purity. Thus the acid phthalates of these substances are readily prepared and may be differentiated by their solubilities and other characters.

By the prolonged heating of a mixture of glycerin with phthalic anhydride or phthalic acid, and distilling the product *in vacuo*, Watson Smith (*J. Soc. Chem. Ind.*, 1901, **20**, 1075) obtained *diglyceryl triphthalate* as a transparent vitreous solid, which softens on heating and may be employed as a cement for glass and porcelain. It is insoluble in almost all solvents, but dissolves to a slight extent in glycerin and acetone.

On heating glyceryl phthalate with resorcinol, *fluorescein* is formed. This is a useful test for the presence of combined phthalic acid.

Qualitative Test.—When phthalic acid (or its anhydride) is fused in a test-tube with a little resorcinol and the product is dissolved in very dilute sodium hydroxide solution, a strongly fluorescent solution (fluorescein) is obtained.

PHTHALIC ANHYDRIDE.
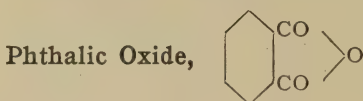
Phthalic Oxide,

Phthalic anhydride is prepared by heating phthalic acid to about $200°$ in a current of air or carbon dioxide, when the anhydride sublimes in long, white, pliant, rhombic needles. It melts at $128°$ and boils at $284.5°$ (thermometer in vapour, Graebe, *Ber.*, 1884, **17**, 1176). Lossen *Annalen*, 1867, **144**, 76) gives the b. p. $276°$. It is only very slightly soluble in cold, but more readily in hot water, and is reconverted into phthalic acid by prolonged boiling with water, more readily in the presence of alkalies.

Gaseous ammonia combines readily with phthalic anhydride on warming, forming *phthalimide*, $C_6H_4\!\!<\!\!{}^{CO}_{CO}\!\!>\!\!NH$ or $C_6H_4\!\!<\!\!{}^{C(NH)}_{CO-}\!\!>\!\!O$, which melts at $233.5°$ (Corr.) (Graebe).

Phthalic anhydride is manufactured extensively for the preparation of the class of colouring-matters known as *phthaleins*, of which the various eosins and rhodamine are examples. It is also used in the manufacture of synthetic indigo.

COMMERCIAL "PHTHALIC ACID."

Commercial "phthalic acid" is the anhydride, and forms beautiful long, flat needles, obtained by a process of sublimation. A good com-

mercial article should form magnificent flat needles, melt at 128°, be completely soluble in benzene, and volatilise completely at a gentle heat.

Tests for Impurities.—1 grm. of phthalic acid should on heating leave behind no weighable residue. A solution of 1 grm. of phthalic acid in 25 c.c. of boiling water should only give the very faintest opalescence (absence of hydrochloric acid). The following test is given by Messner in Lunge's *Chem. Tech. Unt. Meth.*, Vol. 3, 5th Ed. for chlorine compounds (this and the preceding test are of most importance in the case of phthalic acid prepared from naphthalene by means of the tetrachloride). 0.5 grm. of phthalic acid is mixed with 1 grm. of calcium carbonate, free from chlorine, moistened with water, dried and ignited. The residue is dissolved in nitric acid and water so as to give a volume of 20 c.c., and the solution tested with silver nitrate. There should be only a faint opalescence. To test for benzoic acid in phthalic acid, the latter (1 grm.) is shaken with 20 c.c. of benzene and the solution filtered. On evaporating the benzene no residue should remain. As phthalic anhydride is soluble in benzene, before applying this test it must be converted into the acid by dissolving in hot water, evaporating and drying at 100°.

Quantitative Estimation.—1 grm. of the acid or anhydride is dissolved in 20 c.c. of N-sodium hydroxide solution and the solution titrated back with N-hydrochloric acid. 1 c.c. of N-alkali = 0.0830 grm. phthalic acid or 0.0740 grm. of the anhydride.

PHTHALEINS.

The phthaleins are compounds produced by the action of phthalic acid or anhydride on phenols, with elimination of water. Thus, at a moderate temperature, 2 molecules of ordinary phenol act upon one of phthalic acid or anhydride to form *phenolphthalein:*

$$C_6H_4 \begin{matrix} CO.OH \\ \\ CO.OH \end{matrix} + 2\,C_6H_5.OH = \begin{matrix} C_6H_4 \\ | \\ CO.O \end{matrix} \Big\rangle C \begin{matrix} C_6H_4.OH \\ \\ C_6H_4.OH \end{matrix} + 2H_2O.$$
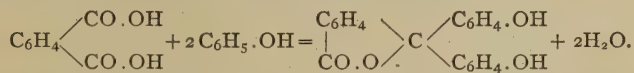
The action is generally carried out by condensing the 2 substances in presence of conc. sulphuric acid or tin chloride at 115 to 120°. When equimolecular proportions of phenol and phthalic anhydride are heated with sulphuric acid at higher temperatures (above 150°) a different action occurs, the two isomeric *hydroxyanthraquinones* being formed.

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$$\text{C}_6\text{H}_4\!\!\begin{array}{c}\diagup\text{CO}\diagdown\\\diagdown\text{CO}\diagup\end{array}\!\!\text{O} + \text{C}_6\text{H}_5.\text{OH}$$

CO OH

$+\text{H}_2\text{O}$

CO

α-Hydroxyanthraquinone.

CO

OH $+\text{H}_2\text{O}$

CO

β-Hydroxyanthraquinone.
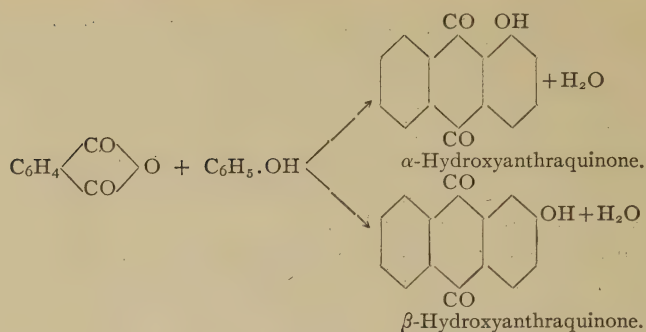
Similarly, when resorcinol, $\text{C}_6\text{H}_4(\text{OH})_2$, is heated with excess of phthalic anhydride to about 200° for half an hour, the mixture acquires a yellowish-red colour, and contains *fluorescein*, $\text{C}_{20}\text{H}_{12}\text{O}_5$, the anhydride of *resorcinol-phthalein*. The melt dissolves in dilute sodium hydroxide or ammonia with dark red colour, the solution changing on dilution to reddish-yellow and yellow, and exhibiting after dilution a fine yellowish-green fluorescence, which is visible in solutions so weak as to appear colourless by transmitted light. On acidifying the solution and agitating with ether, the fluorescein is taken up, and will be again dissolved on agitating the ethereal solution with caustic soda. If phloroglucinol be substituted for resorcinol a yellow liquid is obtained, while pyrogallol yields a blue; but neither is fluorescent. The blue colour due to pyrogallol may be destroyed by cautious addition of permanganate, which acts only slowly on fluorescein. *Catechol-phthalein*, formed by gently heating catechol with phthalic anhydride and a little sulphuric acid, dissolves in sodium hydroxide solution with a fine blue colour.[1] *Quinol-phthalein* is prepared in a similar manner from quinol.

As a class, the phthaleins are weak acid substances which are nearly insoluble in water, but soluble in alcohol and readily so in ether. Their salts with the alkali metals are soluble and strongly coloured. By the action of nascent hydrogen, the phthaleins are reduced to the corresponding *phthalins* (see below) which are colourless substances capable of absorbing oxygen from the air and regenerating the phthaleins.

[1] In the last edition (Vol. 2, part iii, p. 131), quinol-phthalein and quinizarine were spoken of as being identical; quinizarine is 1 : 4-dihydroxyanthraquinone,

$$\text{C}_6\text{H}_4\!\!<\!\!\begin{array}{c}\text{CO}\\\text{CO}\end{array}\!\!>\!\!\text{C}_6\text{H}_2(\text{OH})_2.$$
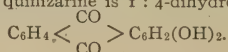
Commercial name	Chemical name or nature	Formula (lactone form)
Phenolphthalein (Purgen, l a x o i n, laxatol)	Phenolphthalein.......	C_6H_4 | $CO.O$ $\Big\rangle C \Big\langle$ $C_6H_4.OH$ $C_6H_4.OH$
Resorcinolphthalein .	Resorcinolphthalein....	C_6H_4 | $CO.O$ $\Big\rangle C \Big\langle$ $C_6H_3(OH)_2$ $C_6H_3(OH)_2$
Fluorescein..........	Anhydride of resorcinol-phthalein	C_6H_4 | $CO.O$ $\Big\rangle C \Big\langle$ $C_6H_3(OH)$ $C_6H_3(OH)$ $\Big\rangle O$
Eosin..............	Tetrabromofluorescein .	
Erythrosin..........	Tetraiodoeosin	
Rhodamines.........	Various phthaleins derived from *m*-amino-phenol.	*e. g.,* C_6H_4 | $CO.O$ $\Big\rangle C \Big\langle$ ... NH Et / O / NH Et Colourless form of diethyl-rhodamine.
Quinolphthalein	Quinolphthalein.......	C_6H_4 | $CO.O$ $\Big\rangle C \Big\langle$ ... OH / O / OH
Gallein.............	Pyrogallolphthalein anhydride, $C_{20}H_{12}O_7$.	C_6H_4 | $CO.O$ $\Big\rangle C \Big\langle$ $C_6H_2(OH)_2$ $C_6H_2(OH)_2$ $\Big\rangle O$
Cœrulein...........	Double anhydride of pyrogallolphthalein, $C_{20}H_{10}O_6$.	... O ‖ ... OH / C / O CO — OH OH

The table on page 547 shows the composition of some of the principal phthaleins, the formula given representing in each case the structure of the colourless lactone form. The eosins, rhodamines, etc., will be dealt with more fully in Vol. 5. Phenolphthalein, gallein and cœrulein are described below.

PHENOLPHTHALEIN, $C_{20}H_{14}O_4 = \dfrac{C_6H_4}{CO.O} \Big\rangle C \Big\langle \dfrac{C_6H_4.OH}{C_6H_4.OH}$
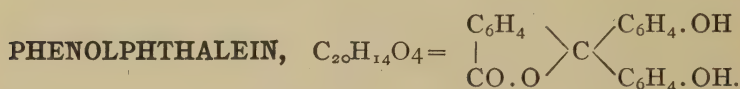
Preparation and Properties.—Phenolphthalein is prepared by heating together 5 parts of phthalic anhydride, 10 of phenol, and 4 of concentrated sulphuric acid during 10 hours at 120°.

The product is boiled with water, and the residue dissolved in dilute sodium hydroxide. On filtering the liquid, the anhydride remains behind, while the phenolphthalein itself is precipitated on treating the filtrate with acetic acid and a little hydrochloric acid. It may be purified by dissolving in alcohol, boiling with animal charcoal, and reprecipitating by diluting the liquid with boiling water.

Phenolphthalein on crystallisation from alcohol is obtained in colourless crusts, melting at 250°. It is only slightly soluble in water, but is readily dissolved by alcohol and ether. In solutions of alkalimetal hydroxides and carbonates, it dissolves with deep red colour.

Silver nitrate gives a violet precipitate with a solution of phenolphthalein.

On treatment with sodium hydroxide and zinc dust, phenolphthalein assimilates 2 atoms of hydrogen, and is reduced to *phthalin*, or *p-dihydroxy-triphenyl-methane-o-carboxylic acid,*

$$CO_2H.C_6H_4.CH \Big\langle \dfrac{C_6H_4.OH}{C_6H_4.OH}$$

This substance forms small needles melting at 225°, and is soluble in alkali hydroxides without colour, but its alkaline solution is immediately turned red by adding potassium ferricyanide, owing to the formation of phenolphthalein.

Phenolphthalein is not used in dyeing. It finds some use in medicine as a laxative, in doses from 1 to 5 grains (0.05 to 0.3 grm.), and is sold under the names *purgen, laxoin, laxatol,* and *laxen.* Its chief interest,

however, is as an indicator of neutrality, for which application it is invaluable.

Structure of Phenolphthalein and its Salts.

$$C_6H_4 \diagdown C \diagup C_6H_4.OH$$
$$CO.O \diagup \diagdown C_6H_4.OH$$

Free phenolphthalein (colourless)

I

$$CO_2H.C_6H_4. \ C$$
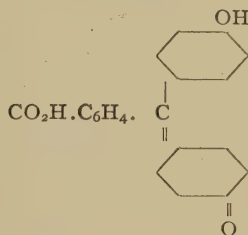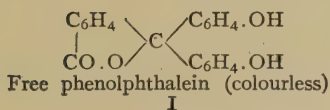
Phenolphthalein in its salts (quinonoid form)

II

$$CO_2H.C_6H_4.CH \diagup C_6H_4.OH$$
$$\diagdown C_6H_4.OH$$

Phthalin

III
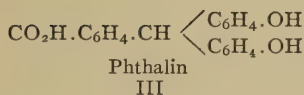
Formula I represents the colourless form of phenolphthalein as a lactonic derivative of triphenylcarbinol. Its close relationship with the triphenylmethane series is clear from its giving phenol-phthalin (Formula III) on reduction. While there is little doubt that formula I correctly represents the structure of free phenol-phthalein, there has been much discussion as to the constitution of its salts, which differ from the colourless parent substance in being highly coloured. Ostwald suggested in explanation of the striking fact that the salts are coloured, that, whereas phenolphthalein itself is non-dissociated in solution, existing in the molecular state, the salts are dissociated and that the negative ion is the source of the colour. In aqueous solution the dissociation

Phenolphthalein$\rightleftarrows C_{20}H_{13}O_4'(red)+H\cdot$
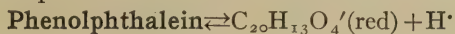
is so slight that the solution appears practically colourless. If a strong base, such as potassium hydroxide, be added, the OH'-ions of the base combine with the H·-ions of the indicator to form water and the equilibrium expressed by the equation given above is destroyed. More phenolphthalein then dissociates until sufficient $C_{20}H_{13}O_4'$-ions have been formed to produce a red colouration.

This explanation, although plausible, fails to explain the real diffi-culty, namely, why the colourless acid should have a coloured ion, and is weakened in value by the fact that the evidence for the existence of a

common coloured ion even in the case of solutions of different salts of
the same metal (for example, copper) is by no means conclusive. (For
a discussion of this point in full see Kayser's *Handbuch der Spektro-
skopie.*) The theory of Ostwald seems, indeed, no longer tenable in
view of the recent work of Green and King (*Ber.*, 1906, **39,** 2365; 1907,
40, 3724. *J. Soc. Chem. Ind.*, 1908, **27,** 3 and 638. Compare R.
Meyer, *Ber.*, 1907, **40,** 3603; 1908, **41,** 2446). Instead, the theory
originally advanced by Nietzki, that a change of structure occurs in
alkaline solution and that the salts of phenolphthalein are derived
from the quinonoid form shown in formula II, appears more correct,
harmonising as it does with modern views as to the origin of colour.
The main fact on which the proof of Green and King depends is, that
it was found possible to prepare coloured *esters* of phenolphthalein, of
the type
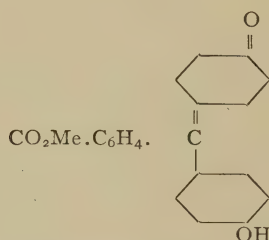
(Phenolphthalein methyl ester.)   Coloured.

Previously all attempts to prepare esters had given merely the colour-
less lactone *ethers.*

Phenolphthalein as an Indicator.—In the last edition, a some-
what general discussion of indicators was included under the heading
"Phenolphthalein." In view of the fact that this subject is now
dealt with fully in several works on general analytical chemistry (for
example, in Lunge's "Technical Methods of Chemical Analysis";
Sutton's "Volumetric Analysis"), the subject will here be considered
only briefly.

According to Ostwald's theory, already referred to, indicators are
substances which possess a coloured ion. In the case of phenolphtha-
lein the action supposed to occur in the presence of a trace of alkali
has already been discussed. The colourless phenolphthalein is sup-
posed to be a weak acid which is practically undissociated in solution.

In presence of a trace of alkali (OH'-ions) red negative ions, $C_{20}H_{13}O_4'$, are liberated. The objections to this view have already been referred to. In the case of methyl-orange, a fairly strong acid (methyl-orange is the sodium salt of dimethylaminobenzenesulphonic acid), the "molecule" is assumed to be red and the negative ion yellow. The colour of the aqueous solution is a mixture of the two colours. The addition of a base intensifies the yellow colour by increasing the number of negative ions, owing to the union of the OH'-ions with the H·-ions of the indicator. When an acid is present the added H·-ions diminish the ionisation of the indicator and thus increase the red colour of the acid molecule. Owing to the relatively strong acid character of methyl-orange, with weak acids the number of H·-ions is too small to produce a visible change of colour until a large excess of acid has been added. For weak acids, therefore, methyl-orange is not a suitable indicator: carbonic acid and hydrogen sulphide do not show an acid reaction with this indicator. On the other hand, in titrating weak bases the strong acid character of methyl-orange makes it very suitable for use. In the case of litmus, the ionic theory gives an explanation similar to that adopted in the case of methyl-orange. The molecule of the litmus acid (azolitmic acid) is supposed to be red and the anion of the alkali salt to be blue. The colour of the aqueous solution of the indicator is a mixed shade intermediate between the two, owing to the dissociation being only slight. As the strength of the litmus acid is supposed to be intermediate between that of the acids of phenolphthalein (very weak) and methyl-orange (relatively strong), the properties of litmus as an indicator are intermediate between those of these two substances.

The alternative theory of indicators, which is more in accord with recently observed facts and the theory of colour than the ionic theory, assumes that in the case of indicators the free acid of the indicator has one colour (in the case of phenolphthalein it is colourless) and the salt of this acid another. The case of the colourless phenolphthalein is slightly abnormal because in the formation of the coloured salt a change of structure (to the quinonoid form) occurs. With methyl-orange, however, the case is simpler, the acid being red and the alkali salts yellow. With indicators, such as p-nitrophenol, a similar very great difference exists between the colour of the free acid and that of the alkali salts: a change of structure has also been assumed to occur here.

Whatever theory of indicators be adopted, the suitability of a certain indicator for titrating a given acid or base depends primarily on the "strength"[1] of the acid titrated relatively to that of the acid of the indicator.

The different behaviour of various indicators has been explained from this point of view (*Ann. Chim. Ph.*, 1885, [vi], **6**, 506) by Berthelot, who has pointed out that an acid which can be accurately titrated with methyl-orange, a relatively strong acid, is one of which the heat-formation exceeds 10.2 calories. Phenolphthalein, on the other hand, which is a very feeble acid, enables any acid to be titrated the heat formation of the potassium salt of which exceeds 6 to 7 calories. With Poirrier's soluble blue still weaker acids can be titrated, but the lower limit of its applicability has not been ascertained, and its indications are in many cases disturbed by dissociation.[2]

R. T. Thomson has investigated the general behaviour of indicators of neutrality in a very complete manner, and arranges the various indicators in 3 groups,[3] to which Allen added *Poirrier's soluble blue*, CLB, as a fourth, thus:

(A) Methyl-orange group	(B) Litmus group	(C) Phenolphtha- lein group	(D) Poirrier's sol- uble blue
Methyl-orange......	Litmus.........	Phenolphthalein....	Soluble blue, CLB.
Cochineal..........	Phenacetolin....	Turmeric..........	....
Congo-red..........	....	Rosolic acid.......	....
Lacmoid...........	....	....	....
Iodeosin	....	....	....
Dimethyl-amino-azo- benzene.	....	....	....

Broadly, the indicators of the methyl-orange group do not react with any but acids of strong affinity, but are sensitive to bases of feeble affinities, such as are many alkaloids. Litmus is often an uncertain

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[1] This word is used here in its modern chemical sense, which must not be confused with the *concentration* of the acid.

[2] R. Engel states that about 85% of the hydrogen of H_3PO_4 and H_3AsO_4 is indicated by Poirrier's blue; while concentrated solutions of KBO_2, K_2PHO_3, K_2PHO_2, KCN, and K_2CO_3 were found to be approximately neutral. Phenol and chloral behave as monobasic acids and resorcinol as a dibasic acid, and all three can be accurately titrated with Poirrier's blue.

[3] For details of the behaviour of these various indicators, Allen's paper on "Neutrality" should be consulted (*Analyst*, **17**, 186, 215; and *Pharm. Journ.* [iii], **22**, 752, 772). See also G. H. A. Clowes, *Amer. J. Pharm.*, 1904, page 453; Cohn's *Treatise on Indicators and Test-papers;* Glaser's monograph (Wiesbaden, 1901); the article by R. Engel, in Moissan's *Traité de Chimic Minérale*, 1904, **3**, p. 494, and the works already cited.

indicator of neutrality, as the point at which the change of colour occurs does not in all cases correspond sharply with the formation of any definite salt. Phenolphthalein is a very delicate and sensitive indicator for the strongest as well as for most very feeble acids.

When intended for use as an indicator, phenolphthalein should be employed as a 1% solution in alcohol. A few drops of this solution, which keeps perfectly, should be added to the liquid to be titrated. The alkali employed may be potassium or sodium hydroxide, but it is important that it should be free from carbonate. Hence barium hydroxide is to be preferred in many cases, since the insolubility of barium carbonate in water ensures the freedom of the solution from that compound. The formation of an insoluble barium salt (e. g., sulphate, oxalate, tartrate) in the liquid is rather an advantage than otherwise, as the pink colouration which marks the completion of the titration is observed with greater facility against the white precipitate than against white porcelain or other external background.

Ammonia is not a suitable alkali for use in conjunction with phenolphthalein. Owing to the formation of *phenol-di-iminophthalein*, $C_{20}H_{16}N_2O_2$, a substance giving a colourless solution with alkalies, the results in presence of ammonia are erratic. An approximation to the truth can be obtained by operating at as low a temperature as possible, and employing a large amount of the indicator, but the results are less satisfactory than those readily obtainable by the use of other indicators (see J. H. Long, *Amer. Chem.*, 1889, **11,** 84; *Analyst*, 1890, **15,** 38, 52).

With the aid of phenolphthalein, the great majority of acids can be accurately titrated in aqueous solution. The end of the change is well defined, especially when the titration is from acid indication to alkaline.

Phenolphthalein is particularly valuable for the titration of comparatively feeble acids, the soluble normal salts of which exhibit an alkaline reaction to litmus. In the majority of cases, the point of neutrality with phenolphthalein is reached when sufficient alkali has been added to replace all the basic hydrogen of the acid, but in other cases the neutral point is attained when $1/2$ or $2/3$ of this amount of alkali has been added.

Such feeble acids as carbonic and sulphydric can be titrated with phenolphthalein, the point of neutrality in cold solutions being indicated by the formation of the compounds $NaHCO_3$ and $NaHS$, re-

spectively. On the other hand, aqueous solutions of silicic and boric acids are wholly indifferent to phenolphthalein, so that the whole of the base present as a silicate or borate is indicated on titration with a mineral acid. In presence, however, of a sufficient proportion of glycerol (not less than 30%) R. T. Thomson has made the valuable observation that boric acid can be titrated by means of phenol-phthalein, the salt $NaBO_2$ being neutral to that indicator under these conditions.

An important advantage possessed by phenolphthalein is that it reacts perfectly in alcoholic solution, and hence allows of the accurate titration of many insoluble or sparingly soluble organic acids, including benzoic, salicylic, palmitic, stearic, oleic, ricinoleic,[1] the acids of colophony, etc.

In many cases (as in the estimation of benzoic acid in paregoric) phenolphthalein may be conveniently employed with an ethereal solution of the acid to be titrated.

Although phenol and other substances containing an OH group have many of the properties of acids, they do not indicate this character to phenolphthalein. This is true of morphine, the molecule of which contains a hydroxyl group having a phenolic function, which enables it to form compounds with the alkalies, and is the cause of its solubility in alkali hydroxides and lime-water.

In the table given below, which has been enlarged from one compiled by R. T. Thomson (*J. Soc. Chem. Ind.*, 1887, **6,** 198), the figures represent the number of atoms of basic hydrogen displaced by sodium or potassium in the form of alkali hydroxide, when a compound is formed showing neutrality to the indicator in question. Thus when methyl-orange is used in the titration of sulphurous acid the neutral point is reached when sodium hydroxide has been added in quantity sufficient to form the compound $NaHSO_3$; but when phenolphthalein is used, the point of neutrality corresponds to the salt Na_2SO_3. Similarly, NaH_2PO_4 is neutral to methyl-orange, Na_2HPO_4 to phenol-phthalein, and Na_3PO_4 to Poirrier's blue.

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[1] In the case of the higher fatty acids, titration in alcoholic solution is necessary not only because the acids themselves are insoluble in water, but also owing to the fact that water effects partial decomposition of their alkali-metal salts (soaps).

BASICITY OF ACIDS AS SHOWN BY DIFFERENT INDICATORS WHEN TITRATED IN AQUEOUS SOLUTION WITH FIXED ALKALI HYDROXIDE.

Acid		Methyl-orange	Phenol-phthalein		Litmus		Poirbier's blue
Name	Formula	Cold	Cold	Boiling	Cold	Boiling	Cold
Hydrochloric....	HCl[1]	1	1	1	1	1	1
Nitric..........	HNO$_3$	1	1	1	1	1	1
Nitrous........	HNO$_2$	Indicator destroyed	1	—	1	0	?
Sulphuric......	H$_2$SO$_4$	2	2	2	2	2	2
Sulphurous.....	H$_2$SO$_3$	1	2	—	—	—	2
Thiosulphuric...	H$_2$S$_2$O$_3$	2	2	2	2	2	—
Sulphydric.....	H$_2$S	0	1 (dilute)	0	—	0	?
Boric	H$_3$BO$_3$	0	—	—	—	—	1
Carbonic.......	H$_2$CO$_3$	0	1 (dilute)	0	—	0	2
Silicic..........	H$_4$SiO$_4$	0	—	—	—	—	?
Phosphoric.....	H$_3$PO$_4$	1	2	—	—	—	3 (nearly)
Arsenic........	H$_3$AsO$_4$	1	2	—	—	—	3 (nearly)
Arsenious......	H$_3$AsO$_3$	0	—	—	0	0	3
Chromic........	H$_2$CrO$_4$	1	2	2	—	0	?
Acetic.........	HC$_2$H$_3$O$_2$	—	1	—	1 (nearly)	—	1
Butyric........	HC$_4$H$_7$O$_2$	—	1	—	1 (nearly)	—	1
Valeric.........	HC$_5$H$_9$O$_2$	—	1	—	1 (nearly)	—	1
Lactic.........	HC$_3$H$_5$O$_3$	—	1	—	1	—	1
Oxalic.........	H$_2$C$_2$O$_4$	—	2	2	2	2	2
Succinic........	H$_2$C$_4$H$_4$O$_4$	—	2	—	2 (nearly)	2	—
Tartaric........	H$_2$C$_4$H$_4$O$_6$	—	2	—	2	—	2
Citric..........	H$_3$C$_6$H$_5$O$_7$	—	3	—	—	—	3
Carbolic (phenol)	HC$_6$H$_5$O	0	—	—	0	—	1
Picric..........	HC$_6$H$_2$N$_3$O$_7$	—	1	1	—	—	1
Benzoic........	HC$_7$H$_5$O$_2$	—	1	1	1	—	1
Salicylic........	HC$_7$H$_5$O$_3$	—	1	1	1 (nearly)	—	1
Hydrocyanic....	HCN	0	0	—	0	—	1
Hydroferrocy-anic.	H$_4$C$_6$N$_6$Fe	4	4	—	4	—	—
Hydroferricyanic	H$_3$C$_6$N$_6$Fe	3	3	—	3	—	—
Thiocyanic.....	HSCN	1	1	—	1	—	1
Uric...........	H$_2$C$_5$H$_2$N$_4$O$_3$	0	1	1	—	—	?

While phenolphthalein is a delicate indicator even for feeble acids, it is absolutely indifferent to the great majority of organic bases, including even aniline and pyridine. The mydriatic alkaloids (atropine, homatropine, hyoscine, and hyoscyamine) form notable exceptions, the aqueous solutions of the free bases strongly reddening phenolphthalein. This property, however, does not exist in alcoholic solution, a fact which marks a curious distinction between these alkaloids and the mineral alkalies, the alcoholic solutions of which react perfectly with phenol-

[1] H Br, HI, and HF (probably) behave like HCl.

phthalein.   According to E. Leger, cicutine (from *Cicuta virosa*) and
codeine are also exceptions to the general rule of indifference of the
alkaloids to phenolphthalein, and P. C. Plugge states that coniine and
nicotine also exhibit an alkaline indication.   As a consequence of the
indifference of most alkaloids to phenolphthalein, their salts react with
this indicator as if the acids were uncombined, and hence the amount
of acid in salts of aconitine, cinchonine, brucine, strychnine, morphine,
quinine, quinidine, urea, etc., operating if necessary in alcoholic
solution, can be ascertained by titration with standard alkali just as if
no organic base were present.

Until comparatively recently, the behaviour of the alkaloids with in-
dicators had been very incompletely studied, and their titration with
standard acid was rarely attempted.   Where this is desired, phenol-
phthalein is inapplicable for their direct estimation, in nearly all
cases; good results are, however, obtained with sparteine and fair
results with coniine (Kippenberger, *Zeit. anal. Chem.*, 1900, **39**, 201).

Kippenberger (*loc. cit.*) has recently studied the degree of accuracy
obtainable in the case of different alkaloids by direct titration in the
presence of various indicators.   The following table taken from the
results, gives the most suitable indicator for use in each case.

> *Atropine:* Lacmoid, uranin.
> *Morphine:* Cochineal, lacmoid.
> *Aconitine:* Azolitmin (litmus).
> *Veratrine:* Lacmoid.
> *Thebaine:* Iodeosin, cochineal.
> *Codeine:* Iodeosin, lacmoid.
> *Emetine:* Iodeosin, cochineal.
> *Cocaine:* Lacmoid.
> *Strychnine:* Azolitmin.
> *Brucine:* Cochineal.
> *Nicotine:* Lacmoid, iodeosin.
> *Coniine:* Iodeosin, cochineal, lacmoid.
> *Sparteine:* Hæmatoxylin.
> *Quinine:* Azolitmin, hæmatoxylin.
> *Pelletierine* (*punicine*)*:* Cochineal.
> *Papaverine:* Lacmoid.
> *Narcotine:* Lacmoid.
> *Narceine* and *caffeine:* None suitable.

The remarkably delicate indicator iodeosin (erythrosine), which
was introduced by Mylius and Förster (*Ber.*, 1891, **24**, 1482) as a
means of estimating the minute traces of alkali dissolved away from
glass by the action of water, is particularly useful as an indicator
in the titration of alkaloids, as for instance in Toth's method of esti-

mating nicotine in tobacco. The methods used in dealing with alkaloids will be described in detail in Vol. 6.

Tetraiodo-phenolphthalein, $C_{20}H_{10}I_4O_4$, is obtained by the direct action of iodine on a solution of phenolphthalein. It forms a pale yellow, odourless, tasteless powder, melting at $255°$ with decomposition and evolution of iodine. It is insoluble in water or alcohol, but is dissolved by ether and chloroform. It combines with alkalies to form soluble salts.

Tetraiodo-phenolphthalein contains 60% of iodine, which is not liberated by the action of alkalies or dilute acids, even on boiling. It is employed in medicine under the name of "*Nosophene*," and has been found valuable in skin-diseases. "*Antinosin*," the sodium salt of nosophene, is a bluish powder which is readily soluble in water, and has been found useful as an antiseptic dusting powder and internally in catarrh of the stomach and intestines.

"**Endoxine,**" the bismuth salt of tetraiodo-phenolphthalein, is a brownish-red, odourless and tasteless powder, soluble in alkalies with bluish-violet colour. It is employed as an internal antiseptic.

Gallein, $C_{20}H_{12}O_7$, obtained by heating pyrogallol and phthalic anhydride to $190°$ to $200°$, forms a brownish-red powder, or green crystals of metallic lustre which are almost insoluble in water, but soluble in alcohol. Gallein is a weak acid, forming with alkalies a blue solution which becomes dirty-coloured on standing. Gallein dissolves in ammonia with violet colour, and the solution gives violet precipitates with metallic salts.

When heated at $200°$ with 20 times its weight of strong sulphuric acid, gallein loses the elements of water and is converted into:

Cœrulein, $C_{20}H_{10}O_6$, which on pouring the cooled solution into water is obtained as an amorphous black precipitate. It is nearly insoluble in water (which it colours olive-brown), alcohol, or ether, but dissolves easily in acetic acid. In commerce, cœrulein occurs as a thick dark coloured paste. In alkalies it dissolves with beautiful grass-green colour, and the solution gives with mordants very stable lakes. With strong sulphuric acid cœrulein gives a dirty brown colour. On warming cœrulein with ammonia and zinc powder, a brownish-red solution is formed, containing *cœrulin*, $C_{20}H_{12}O_6$. The solution is oxidised on exposure to air, the original green colour being restored. Cœrulein may be employed in dyeing in the same manner as indigo.

On treating cœrulein paste with 2 molecules of sodium hydrogen sul-

phite ($NaHSO_3$), a colourless compound of the two is formed, which can be removed from the unaltered cœrulein by extraction with cold alcohol. The bisulphite compound of cœrulein occurs in commerce as a black powder under the name of *Cœrulein S.* It dissolves in water with greenish-yellow colour, and on boiling the solution becomes deep green, and sulphurous acid is evolved. Acids and alkalies effect the same decomposition in the cold.

Cœrulein and its bisulphite compound are used for dyeing and printing cotton fabrics, on which they produce various shades of green. The colour is not removed from the fibre by boiling soap or alkali hydroxides and is darkened by concentrated hydrochloric acid. The most characteristic test for cœrulein is that with a warm acid solution of stannous chloride, which turns the fibre brownish-red owing to the formation of cœrulin. On then washing with water, or preferably with a very dilute solution of bleaching-powder, the original green colour is restored.

MODERN EXPLOSIVES.

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Until the latter part of the nineteenth century the only explosive used commercially was black gunpowder, a mixture of saltpetre, charcoal, and sulphur. Although large quantities of this are still used, its manufacture must be looked upon as a dying industry, as it is being displaced by modern explosives, the most important constituents of which are organic compounds containing nitrogen and oxygen. The principal of these are nitro-derivatives from cotton, glycerol, and aromatic hydrocarbons.

Modern explosives may be divided into two classes: propellants and blasting explosives. The former are used for driving projectiles from a firearm, the latter for shattering rocks, etc.

The old black powder mixture was used for all purposes, for small arms or the largest cannon and for blasting, although in comparatively modern times changes were introduced, especially in the methods of preparing the charcoal and granulating the powder to fit the material for the different purposes. Modern explosives, however, differ in composition as well as form and method of manufacturing according to the purpose for which they are intended, and an explosive which is intended for one purpose cannot, as a rule, be used for another.

Propellant explosives may again be divided into two divisions: those used in smooth-bore sporting guns and those for rifled firearms. The latter are, of course, used in very large quantities for warlike purposes by all nations, and have formed the subject of numerous investigations by commissions and the official and other chemists of all the great powers. These researches have been directed not only toward finding the most powerful and effective explosives, but also toward ascertaining which are the most safe in use and storage, and to devising

tests which will show whether the explosive has been rendered thoroughly stable. As the carrying out of these tests forms an important part of the chemical examination of explosives, descriptions of the principal ones are given below.

CELLULOSE NITRATES.

The form of cellulose used for the manufacture of explosives and celluloid is almost exclusively cotton, although wood cellulose has been used. All commercial nitrocellulose is made by nitrating with a mixture of nitric and sulphuric acids, in which the latter usually predominates. The nitration is sometimes carried out in earthenware pots immersed in cold water, the acid being afterward wrung out in centrifugal machines, and sometimes the nitration itself is carried out in special centrifugal machines, but recently Sir F. L. Nathan and the Messrs. Thomson, of the Royal Gunpowder Factory, Waltham Abbey, have introduced a new method known as "the displacement process," in which centrifugal machines are dispensed with, and the acids are entirely removed by gradual displacement with water (Eng. Pat. 7269, 1903). The stability and nature of the nitrocotton are considerably affected by the method used in its manufacture, as also by the quality of cellulose employed, and other details of preparation. After nitration the material is thoroughly washed, boiled for some days with frequent changes of water (see Robertson, *J. Soc. Chem. Ind.*, 1906, **25,** 624) and pulped in a machine resembling a papermaker's poacher or beating engine.

Properties of Nitrocellulose.—The true sp. gr. is given by Mosenthal as 1.65 to 1.68 (*J. Soc. Chem. Ind.*, 1906, **26,** 443). Ordinary compressed blocks containing much water and air have a sp. gr. of 1.0 to 1.2, but if highly compressed for blasting purposes it may be as high as 1.4. The compressed material resembles wood pulp. When it has been gelatinised with a solvent it resembles horn, but is tougher and harder. It is slowly saponified by alkalies. It is reduced to cellulose by potassium and ammonium hydrosulphides, sodium stannate, sulphides, polysulphides, and thiocarbonates. It is somewhat hygroscopic. Will showed that if n is the percentage of nitrogen in a sample of nitrocotton, and h the percentage of moisture it takes up in saturated air at $25°$, $n + h = 14.6 \pm 0.1$. Even good nitrocellulose decomposes at all temperatures, giving off carbon monoxide and nitrogen

oxides. The rate of decomposition increases rapidly with rise of temperature, and is doubled for every increase of 5°. (Will).

The cotton used for the manufacture of guncotton for propulsive explosives is usually cotton waste obtained from the sweepings of cotton mills, but it is first subjected to a thorough purification by boiling with sodium hydroxide and bleaching, etc. For the manufacture of cordite for the British Government it is specified that the cotton waste shall not contain more than 8% of moisture or 0.8% of fat, which is determined by extraction with ether in a Soxhlet apparatus. It must also be free from pieces of string, metal, and other foreign matter, and must not leave more than 1% of ash when ignited. It is also very desirable that the material should not contain a large proportion of the fine short fibres of cotton known as "fly," as the presence of these leads to the formation of lower nitrates and unstable compounds.

For the manufacture of collodion cotton for the preparation of blasting gelatine, cotton waste cannot be used, as the resulting nitro-cotton, when dissolved in nitroglycerin, does not produce a sufficiently stiff jelly. It is, therefore, necessary to use a long staple cotton specially prepared, which is much more expensive than cotton waste.

When guncotton is to be used for the manufacture of other explosives it is usually moulded in hydraulic presses into blocks of various shapes containing 30 to 40% of water. When used by itself as a blasting explosive it is compressed strongly until it is as hard as hard wood and contains about 20% of moisture. That used by the British Government is a nitrocotton containing 12.8% of nitrogen mixed with a little phenol and calcium carbonate to prevent decomposition. Small cylinders of the same material, but dried, are also used as primers for firing charges of wet guncotton. Nitrated cotton yarn impregnated with rubber solution is also used as a priming charge for certain sorts of ammunition.

Nitrogen.—According to the strength and composition of the acids and other conditions of nitration, nitrocelluloses can be obtained with very different proportions of nitrogen and differing in many of their properties. It is possible in the laboratory to prepare a gun-cotton containing 14% of nitrogen, which almost agrees with the formula for the trinitrate $C_6H_7(NO_3)_3O_2$, but this compound is very unstable and breaks down even on standing at the ordinary temperature for a few weeks, leaving a lower nitrate. (See Lunge and

Bebie, *J. Soc. Chem. Ind.*, 1901, **14**, 514.) On the manufacturing scale it is hardly practicable to produce a nitrocellulose containing more than 13.5% of nitrogen, and commercial guncotton seldom contains more than about 13%. The guncotton used for making cordite is specified to contain 12.8 to 13.1%. Nitrocottons used for making some other smokeless powders for sporting and military purposes generally contain percentages of nitrogen from 12.4 up to 12.8%. Collodion cotton for blasting gelatine contains 12.0 to 12.3%, for celluloid, varnish, and artificial silk still lower nitrates are used. Various writers have endeavoured to classify nitrocelluloses according to their chemical formulæ; assuming the celluloid molecule to be of some particular size, $C_6H_{10}O_5$ or $C_{12}H_{20}O_{10}$ or $C_{24}H_{40}O_{20}$, they have divided the nitrocelluloses into tri- and di-nitrates, or penta-, tetra-, and tri-nitrates, etc., but as no fixed limits can be drawn between the different classes, and products can be obtained with any desired percentages of nitrogen, it is better to specify the nitrocelluloses according to their percentages of nitrogen, solubility in ether-alcohol, and other properties. (See Sapojnikow, *Zeits. Schiess-Sprengstoffwesen*, 1909, **4**, 441, 462).

Detection of Nitrocellulose.—This depends whether the substance has been gelatinised with a solvent or not. Practically all propellants contain nitrocellulose wholly or partly gelatinised. Many of them consist practically entirely of nitrocotton, and most of them contain at least 50%. The form of cellulose used is almost invariably cotton, but wood cellulose has been employed in the manufacture of Schultze powder and some others. Colloided nitrocellulose can be recognised by its hard, tough nature; unless mixed with liquid material, such as nitroglycerin, it is as tough as horn. It may be distinguished from other substances by the fact that it is insoluble in water, alcohol, or ether, but soluble in acetone and ethyl acetate. The various nitrocottons can be distinguished from one another, after isolation, by the percentage of nitrogen and of matters soluble in a mixture of alcohol and ether.

Ungelatinized nitrocellulose can be recognised by the structure of the fibres, which is almost the same as that of the unnitrated material. There is, however, a distinct difference in colour when the fibres are examined in polarised light.

Estimation of Nitrocellulose.—This is usually done by extracting the explosive with one or more of the solvents, in which nitrocellulose

is insoluble and the weighing the residue of nitrocellulose. The first extraction is nearly always with ether, and in many cases no further extraction is needed. If mineral nitrates are present, a further extraction with water is necessary, and in many cases an extraction with benzene is required to remove organic substances. About 2 grm. of the explosive are weighed out into a filter-paper or thimble and extracted in a Soxhlet with ether (sp. gr. 0.72). The filter-paper and contents are then dried in a water-oven to constant weight, and the weight of the filter-paper or thimble is deducted. The material used for this analysis should be so finely ground, that it passes through the finer sieve of the nest used for the heat test. This material should be allowed to soak in the ether all night and then extracted with it for about 2 hours.

In some cases, if the percentage of nitrogen in the nitrocellulose is known, it may be estimated indirectly by a nitrogen determination.

Examination of Nitrocellulose.—*The estimation of nitrogen* in guncotton is generally carried out by means of a Lunge nitrometer provided with a cup and graduated from about 100 to 150 c.c. It is filled with mercury, the bottom of the tube being connected by means of rubber tubing with canvas insertion to a compensating tube. The guncotton is dried in a water-bath to constant weight, 0.5 grm. or more is weighed out, according to the percentage of nitrogen, precautions being taken that moisture is not absorbed during the weighing, as the material is very hygroscopic. It is then transferred to the cup of the nitrometer, and 5 c.c. of concentrated sulphuric acid are added. The material is stirred from time to time with a small glass rod until it dissolves, which takes about 1/2 hour. Then it is allowed to run into the nitrometer, and is rinsed in several times with sulphuric acid, using for this purpose 10 c.c. The bulb is then shaken vigorously so as to bring the mercury and acid into intimate contact. After a short time nitric oxide is evolved. The shaking is continued until the evolution is practically complete. Then the nitrometer is allowed to stand until the acid and mercury have separated from one another and the shaking is repeated. After standing for about 1/2 hour to cool, the volume is read as also the temperature and barometric pressure, the volume is corrected to N. T. P., and the percentage of nitrogen in the guncotton is calculated. In this as in all operations with the Lunge nitrometer the result depends to some extent on the exact method of shaking, and it is only after some practice that the

operator can obtain results approaching the theoretical. Beginners almost invariably obtain results which are too low.

Berl and Jurrissen carry out the reaction with acid and mercury in a separate vessel and claim that thereby a more accurate result is obtained. (*Zeits. ang. Chem.*, 1910, **23,** 241; *Zeits. Schiess-Spreng-stoffwesen,* 1910, **5,** 61.)

The Schultze-Tiemann method is also used extensively in many laboratories for the estimation of nitrogen. It usually gives results 0.1 or 0.2% higher than the Lunge nitrometer. It is specially useful for the analysis of guncottons that have not yet undergone purification by boiling, as the nitrometer gives very low results for these. They evidently contain some unstable impurities, which interfere with the reaction of the mercury. The following are the details of the method as it is carried out at the Dartford factory of Messrs. Curtis and Harvey:

0.5 grm. of the dry nitrocellulose and 30 c.c. of boiling water are introduced into a flask of about 200 c.c. capacity fitted with rubber cork, through which pass two tubes. One of these leads into the lower end of a graduated tube of 150 c.c. capacity and the other is used to introduce liquid into the flask. Both tubes have rubber connections which can be closed by means of pinchcocks. Air is expelled from the flask and tubes by boiling the water in it energetically for some time, and the pinchcocks are closed. Then the graduated tube is placed in position, 20 c.c. of hydrochloric acid and 20 c.c. of strong ferrous chloride solution are boiled up in a test-tube and then the contents are drawn into the flask, care being taken not to admit any air. A little boiling water is added to wash out the test-tube, the admission tube is closed by means of its pinchcock, the contents of the flask are gently boiled, and the other tube leading to the measuring tube is opened. The gas comes off and passes into the measuring tube, which has been filled with strong sodium hydroxide solution and stands in a bath of the same liquid. The evolution lasts about 15 minutes. Some more boiling water is then run into the flask to wash down any particles of unattacked nitrocellulose and the contents are then boiled again, this procedure being continued until there is no further evolution of gas. The orifice of the graduated tube is then covered with the thumb or finger protected with a rubber finger stall, and removed to a large cylinder containing water, where it is allowed to cool. The tube is adjusted so that the water is at the same level inside and out, the volume of

nitric oxide is then read, corrected for temperature and pressure, and calculated to percentage of nitrogen.

See also Jacqué (Report of Sixth Int. Cong. Ap. Chem., Vol. 1, page 265).

The Dumas method can also be used if precautions are taken to prevent the nitrocellulose from burning too rapidly: it must be mixed with a large quantity of inert material. The method is, however, seldom used for this purpose.

Solubility.—All nitrocelluloses are soluble in acetone, ethyl-acetate, amyl acetate, and some other organic solvents. They are all insoluble in water and benzene, and all but the very low nitrated products are insoluble in either pure ether or alcohol, although commercial nitrocelluloses give up a small amount of fatty matter to ether, and resinous matter and decomposition products to alcohol. It should, however, be noted that commercial ethers usually contain a small proportion of alcohol, and if an ether of this kind be used, some of the nitrocellulose will be dissolved. The sp. gr. of ether used for extracting fatty matter and nitroglycerin from nitrocellulose should not exceed 0.720.

The different nitrocelluloses are characterised by different degrees of solubility in a mixture of ether and alcohol. The highest nitrated products are practically insoluble in the mixed solvents. Guncottons containing 13% of nitrogen give up about 8 or 10%, and as the percentage of nitrogen further falls and the solubility rapidly increases until with nitrocottons containing about 12.3% solubility is practically complete. The degree of solubility is, however, not conditioned solely by the percentage of nitrogen, but also depends upon the proportions of nitric and sulphuric acid used in nitration, and other details of preparation. For further details regarding this, see Lunge and Weintraub (*Zeits., ang. Chem.*, 1899, **12,** 441).

Solubility Determination.—The solubility of a guncotton in etheralcohol depends to a certain extent upon the composition of the solvent used and the other conditions. It is, therefore, necessary to describe the exact method of carrying out the test. For testing the guncotton used in the manufacture of cordite the English War Department lays down the following rules:

50 grains (3.3 grm.) of the air-dry guncotton are weighed out and transferred to a stoppered graduated cylinder of 200 c.c. capacity. A mixture is made of two volumes of ether to one of alcohol, 80%, and 150 c.c. are poured on to the guncotton and occasionally

agitated with it for about 6 hours at 15.5° and then allowed to settle. 75 c.c. of the clear liquid are then transferred to a small weighed flask, the greater part of the ether and alcohol is distilled off, and the remainder is driven off by heating in a drying oven the temperature of which is not more than 49° (120° F.), the drying being continued until the weight is constant. The quantity of soluble matter must not be greater than 12%.

This method cannot fail to give somewhat high results, as the whole of the solvent cannot be driven off in the manner prescribed. This, however, is not a matter of importance as the results are only intended to be comparative. A more serious objection to the test is that the results depend very largely upon the nature of the ether used, and no directions are given for selecting it. Methylated ether contains considerable proportions of ethyl methyl ether and dimethyl ether, which have considerably greater solvent action upon guncotton than diethyl ether; and it also contains alcohol and water in various proportions. Constant results can only be obtained, therefore, if each supply of ether is tested upon a standard sample of guncotton. But even if 2 ethers give the same result with one sample of guncotton, they will not necessarily give the same result with another, which has been made by a different process.

The English official method given above is intended principally for nitrocelluloses, which are only slightly soluble in ethyl alcohol; with those that are almost entirely soluble it is better to weigh the undissolved residue instead of the dissolved matter. For the soluble nitrocellulose used for the manufacture of the United States nitrocellulose powder the official method is as follows:

1 grm. of the finely divided dry sample is treated with frequent stirring, in a covered beaker or other suitable vessel with 350 c.c. of a mixture of pure ethyl alcohol and pure ethyl ether, the sp. gr. of the mixture to be from 0.748 to 0.750 at 20°. The vessel is kept covered to prevent loss by evaporation. The residue is allowed to settle and the supernatant liquid siphoned off. The extraction with ether-alcohol solution is repeated twice: the insoluble residue is poured into a tared Gooch crucible having a thin asbestos filter, and well washed with ether-alcohol. The residue is then partially dried at 80°, and the drying completed by exposure to a temperature of 100° till the weight is constant. The % of insoluble matter subtracted from 100 gives the % of soluble nitrocellulose, which must be at least 95%. If "soluble

nitrocellulose" is to be determined in a nitrocellulose containing considerably less than 95%, the determination is made on 0.5 grm. or less.

Matter Insoluble in Acetone.—The matter insoluble in acetone consists mostly of unnitrated or very imperfectly nitrated fibres. To determine it, 2 grm. are treated with about 150 c.c. of acetone for 6 or 8 hours with occasional shaking. It is then allowed to stand overnight and the clear liquid is carefully decanted off. The residue is washed several times by decantation with acetone, then transferred to a tared filter, washed again, dried in the water-bath, and weighed.

Unnitrated fibre is sometimes estimated by repeated treatment with sodium sulphide solution, which attacks the nitrocelluloses, but leaves the unnitrated cellulose unaffected. Lunge and Weintraub, however, found the method unsatisfactory, and recommend instead the use of sodium ethylate, which acts in a somewhat similar manner. (*Zeits. ang. Chem.*, 1899, **12**, 473). The method is specially useful in the case of products which contain a considerable proportion of matter insoluble in acetone.

In 100 c.c. of ordinary alcohol dissolve 3 grm. of sodium, and if the liquid is not quite clear, filter. Add 100 c.c. of acetone, and of the mixture set aside, 50 c.c. Into the remaining 150 c.c. introduce about 5 grm. of the nitrocellulose. The action is hastened by warming on a water-bath to 40 or 50° with occasional agitation. In 20 or 30 minutes the action is complete; the brownish-red liquid is allowed to settle, and decanted through a small filter-paper, and the precipitate is washed by decantation with alcohol to remove any condensation products of acetone. The brown solid is then removed by treatment with water and the residue is washed, first with hot water, and then with water containing a little hydrochloric acid. If the amount of unnitrated cellulose is considerable or if a high degree of accuracy is not desired, this first treatment may suffice. The cellulose contained evolves no gas in the nitrometer, but gives a strong reaction with diphenylamine, showing that traces of nitrocellulose are still present. It may, therefore, be desirable to repeat the extraction. For this purpose the residue is first washed with alcohol to displace the water, and is then washed off the filter with a 50 c.c. of the acetone ethylate solution set aside as above. The remainder of the above treatment is then repeated and finally the cellulose is washed with water, dried at 100°, and weighed. It now only gives a slight blue colouration with diphenylamine. The cellulose residue should only have a very slight

brown colour, which may be removed by treatment with bleaching solution. A good nitrocellulose contains hardly any unnitrated fibre.

Free Acid and Alkali.—These may be determined by extracting the finely divided material with hot water, filtering, and titrating in the usual way. Very thorough washing is necessary, as the material has the property of adsorbing considerable quantities of acid and alkali. When testing for minute traces it is necessary to carefully examine the water and other materials used.

Nitrocellulose usually contains more or less calcium carbonate, which has either been added intentionally or has been precipitated from the water used for boiling the material during the purification. To determine this digest a known weight of the sample with a known volume of standard hydrochloric acid, filter, wash thoroughly and titrate, using methyl-orange or other suitable indicator.

Discolouration.—Really pure nitrocellulose when ungelatinised is quite white, but it has often a slight brown tint due to oxide of iron precipitated in the fibres during manufacture. When stored in a wet condition it frequently becomes quite black, especially on the surface, in consequence of bacterial action. The bacteria, however, attack mostly the paper or other organic material in contact with the nitrocellulose. This discoloured nitrocellulose generally gives a low heat test.

Ash.—The guncotton is mixed with paraffin wax and paraffin oil in a large crucible, which is set alight, a small flame being kept going underneath. As the mixture burns away, more wax is added from time to time. The flame must not be allowed to come in contact with the guncotton itself until it has been broken down by the heat. Finally the crucible is ignited to destroy all organic matter, cooled and weighed.

Microscopic Examination.—It is best for this to embed the material in Canada balsam or moisten it with 50% alcohol. In polarised light the fibres appear of various colours depending upon the degree of nitration and conditions of manufacture, and can readily be distinguished from unnitrated cellulose and foreign matter. For details of this and other optical properties see Mosenthal (*J. Soc. Chem. Ind.*, 1907, **26**, 1).

Sulphuric Esters.—It was shown by Cross, Bevan, and Jenks (*J. Soc. Chem. Ind.*, 1905, **24**, 379; *Ber.*, 1901, **34**, 2496) that during the process of nitrating cotton a small proportion of mixed sulphuric-nitric esters of cellulose are formed, and it was demonstrated by Hake and Lewis (*J. Soc. Chem. Ind.*, 1905, **24**, 374) that these bodies are

considerably less stable than the pure nitric esters. They are decomposed only very slowly by boiling with alkaline water, but are very readily hydrolised by acid. Hence the necessity of having the first waters acid in the boiling of guncotton (see Robertson, *J. Soc. Chem. Ind.*, 1906, **25**, 624).

To ascertain the amount of combined sulphuric acid in nitrocotton take 5 grm. of it, weigh, and allow it to stand for 48 hours under a bell-jar over strong nitric acid. Then wash with water and estimate the sulphuric acid by precipitation with barium chloride. In a separate portion estimate the amount of mineral sulphate by extracting with water and estimating as barium sulphate in the usual manner and deduct. Instead of nitric acid, glacial acetic acid may be used, but in this case it is necessary to treat with the acid fumes several times.

Viscosity of Solutions of Nitrocellulose.—In the case of collodion cotton to be used in the manufacture of blasting gelatine it is necessary that the solution in nitroglycerin be a stiff semisolid. Different samples of collodion cotton differ very greatly as regards this property. The easiest method for ascertaining whether a given sample will produce a stiff blasting gelatine is to dissolve it in a suitable solvent, and determine the viscosity of the solution. The solvent generally used is either acetone or ether-alcohol. The former dissolves all nitrocelluloses, whereas the latter dissolves practically the same ones as nitroglycerin. A solution of 1% strength or other convenient concentration is made up and allowed to settle. The viscosity is determined by means of a 50 c.c. pipette, with a mark above the bulb and another below it. The time is measured that is required for the surface of the liquid to fall from the upper to the lower mark, when the liquid is running freely from the orifice, the temperature being kept at 15° or other suitable fixed point. The orifice must be adjusted to a suitable size, and then the instrument must be kept carefully for these measurements. The time is compared to that occupied by water to flow from the orifice in the same manner.

An objection to this method is that the orifice is liable to become stopped wholly or partly with particles of fibre. To avoid this some workers prefer to take the time occupied by a small glass bulb to rise through a column of the solution of a given height.

For making blasting gelatine and other similar explosives the viscosity should be high, as already stated. For artificial silk, on the other hand, it should be low, and for some other purposes, such as the

preparation of collodion solution for dipping incandescent mantles, an intermediate value is required.

Stability Tests.—For these see below, end of chapter.

NITROGLYCERIN.

When strong glycerol is gradually added to a well-cooled mixture of very strong nitric and sulphuric acids, it is converted into propenyl nitrate, or nitroglycerin, formerly called "glonoïn oil." When great care is taken, nearly the theoretical yield is obtainable; but if the temperature is allowed to rise, a more complex reaction ensues, with formation of oxalic acid, glyceric acid, etc., and if the action is very violent, spontaneous explosion may take place. This may also occur if the glycerol is impure.

For the latest methods of manufacture see Nathan and Rintoul, (*J. Soc. Chem. Ind.*, 1908, **27,** 193). After separation from the acid mixture the nitroglycerin is washed with water, then with dilute sodium carbonate solution, and finally with water again.

Nitroglycerin is a heavy oily liquid which when pure is colourless, but the commercial product is yellow. Its sp. gr. is 1.60 at 15°, but on freezing it contracts 8.3% of its volume. It is slightly volatile; the vapour tension at 70° was found by Marshall (*J. Soc. Chem. Ind.*, 1904, **23,** 154) to be 0.005 cm. of mercury at 70° which is practically the same as that of mercury. It is not hygroscopic and is almost insoluble in water. It is also insoluble in glycerol and petroleum spirit. It is readily soluble in ether, ethyl acetate, acetone, ethyl and methyl alcohol, chloroform, glacial acetic acid, amyl alcohol, benzene, toluene, nitrobenzene, phenol, olive oil, and sulphuric acid. It dissolves less readily and with partial decomposition in carbon disulphide, nitric acid, and hydrochloric acid (see Elliott, *School of Mines Quarterly*, **4,** 15).

The true freezing-point of nitroglycerin was found by Nauckhoff (*Zeits. ang. Chem.*, 1905, 16) to be 12.3°, but that of the commercial product is frequently some degrees lower in consequence of the presence of dinitroglycerin. Nitroglycerin shows the property of supercooling very markedly, and nitroglycerin explosives can often be kept for long periods at temperatures below 0° without freezing. (See also Kast, *Zeits. Schiess-sprengstoffwesen*, 1906, **1,** 225.)

Solid frozen nitroglycerin is less sensitive to shock than the liquid, but when half frozen it explodes easily, and is consequently very

dangerous; moreover, the freezing of the nitroglycerin in composite explosives tends to cause it to separate from the other constituents and form a liquid layer on the surface when it melts again. This phenomenon, known as "exudation," is also a source of danger. To prevent the freezing of the nitroglycerin it has been proposed to add to it various substances which depress the freezing-point in accordance with van't Hoff's law. Among the substances which have been proposed for this purpose are nitrobenzene, nitronaphthalene, dinitroglycerin, dinitromonochlorhydrin, and nitrates of polymerised glycerol.

Nitroglycerin has a very powerful physiological effect. Merely handling it or entering a house containing it will often give a violent headache to anyone not accustomed to it.

Detection.—If some of the dry explosive (1 to 5 grm.) is placed in a dish on a boiling water-bath, and the dish is covered over with a glass beaker or funnel, after an hour the glass will be found to be clouded with minute drops of nitroglycerin, if any is present. The appearance is very characteristic, and quite distinct from that of the large drops of liquid which may be formed in consequence of the presence of water or organic solvents.

Nitroglycerin can also be detected by extracting with ether, evaporating off the solvent, and examining the residue. If the residue is a viscous liquid readily soluble in 80% methyl alcohol, but insoluble in water, it is probably nitroglycerin. Absorbed by filter-paper and ignited, it will burn quietly with a peculiar green flame.

Examination.—Nitroglycerin as such is not allowed to be transported out of the factory at which it is made, and for extra security it is usual to mix it as soon as possible with guncotton or some other material which renders it less sensitive. Consequently the examination of commercial nitroglycerin is hardly ever carried out, except in the factory.

The percentage of *nitrogen* may be ascertained by weighing out 0.32 to 0.35 grm. into a small beaker, dissolving it in sulphuric acid and introducing it into the Lunge nitrometer, as described above, under Nitrocellulose. The theoretical percentage is 18.53. The results obtained are usually 0.1 to 0.2% lower than this, principally in consequence of the error of the process. If the percentage of nitrogen is very low, it shows the presence of dinitroglycerin or some other impurity.

To determine the alkalinity take 20 grm. shake up with 50 c.c. of water, and titrate with $N/10$ sulphuric acid, using methyl-orange as indicator. For nitroglycerin used in the manufacture of cordite, it is specified that the alkalinity shall not exceed 0.01% calculated as sodium carbonate.

Moisture may be determined by weighing out about 5 grm. into a small dish and allowing it to stand at the ordinary temperature over calcium chloride in a desiccator, which may be evacuated if preferred.

Stability Tests.—The only test usually applied is the Abel heat test, *q. v.* Guttmann's cannot be utilized with explosives containing nitroglycerin.

Estimation.—In consequence of the volatility of nitroglycerin it is not practicable to weigh it after extracting it by means of a solvent from a composite explosive. When possible it is therefore estimated by difference, but in many cases it is very desirable to estimate the nitroglycerin directly. If it is known that no other substance is present, which will evolve nitrogen in the nitrometer the percentage of nitroglycerin can be deduced from a nitrogen determination on the explosive. Or if the amount of nitrogen due to other nitric esters or nitrates is known, it is still possible to calculate the percentage of nitroglycerin. Silberrad, Ablett, and Merryman (*J. Soc. Chem. Ind.*, 1906, **25**, 628) have worked out a method for the direct estimation of nitroglycerin which is as follows:

A weighed quantity of the ground cordite, or other explosive sufficient to yield 1.5 grm. of nitroglycerin, is placed in a thimble in the extractor A (Fig. 19), which is fitted up as shown. 80 c.c. of absolute ether is poured into the flask and extraction is carried out in the usual manner. After the extraction is complete the thimble containing the nitrocellulose, etc., is washed with a little fresh ether, and removed from the extractor, a little ether being left in the latter. The absorption flasks, C, containing 10 c.c. of $N/10$ acid, are now affixed, and excess of sodium ethylate (about 50 c.c. of a solution prepared by dissolving 5 grm. of sodium in 100 c.c. of absolute alcohol) is run into the flask little by little through the side tube D. About 10 c.c. of ethylate solution are also blown up through the stopcock, E, into the extractor. The reaction takes place rapidly and is completed by warming on the water-bath for about 6 hours; its course may be followed by periodically drawing off small samples by means of the tap, E, filtering them and examining them for nitroglycerin by means

of diphenylamine in sulphuric acid. The ether is then distilled up into the extractor and run off by means of the tap, and the apparatus is cleansed of vapour by blowing air through. The residue in the flask is dissolved in water and transferred to a 150 c.c. flask, the wash-

FIG. 19.

ings of the flask and extractor are added, and the volume of liquid is made up to the mark. 50 c.c. of the solution are then transferred to the flask, F, of the reduction apparatus (Fig. 20), 50 grm. of a mixture of powdered zinc (2 parts) and reduced iron (1 part) are

added together with 50 c.c. of 4% sodium hydroxide solution, 60 c.c. of N/10 acid being placed in the absorption flasks, H. After the apparatus has stood in the cold for 1 hour, the contents of the flask F are boiled. After boiling for 1 hour a current of one air is passed through for 1 1/2 hours, boiling being still continued. For the last
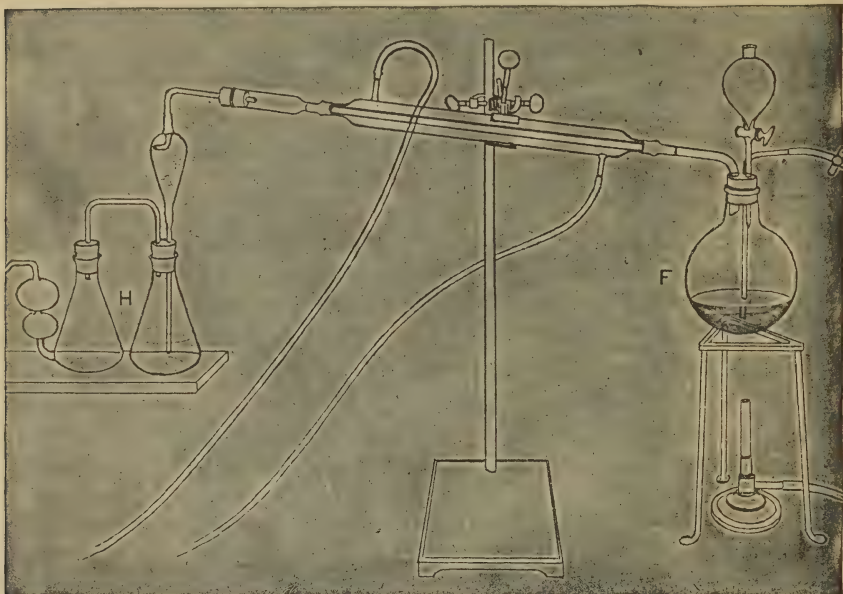
FIG. 20.

1/2 hour there should be no water in the condenser. The excess of standard acid is then titrated back. Each c.c. of N/10 acid corresponds to 0.007567 grm. of nitroglycerin. The experimental error does not exceed 1%.

DINITROGLYCERIN. PROPENYL DINITRATE.

This compound might be made by nitrating glycerin in a similar manner to ordinary nitroglycerin except that a smaller proportion of nitric acid is used. The substance resembles the trinitrate in most respects, but is readily soluble in mineral acids and water. This causes considerable difficulties in the separation from the acids and in the purification, and it is necessary to have recourse to some elaborate

process, such as diluting the acids with water, then neutralising with calcium carbonate and extracting with ether, and then distilling off the ether. (See Escales, "Nitroglyzerin und Dynamit," page 180, Leipzig, 1908.)

Dinitroglycerin is a colourless or light yellow, odourless oil, sp. gr. 1.47 at 15°. Under 15 mm. pressure it boils constantly at 146°. It freezes to a glass-like mass at temperatures under −30°. It dissolves in about 20 parts of water at 15°, and more readily in dilute acid. It is less easily exploded than ordinary nitroglycerin either by blow or heat. It gelatinises collodion cotton even in the cold. A mixture with an equal quantity of trinitroglycerin remains liquid at −20°, a mixture with two parts freezes at −12°. It is not quite such a powerful explosive as nitroglycerin.

MIXED ESTERS OF GLYCEROL.

These could be made by the action of acids, such as hydrochloric, acetic, or oxalic, upon dinitroglycerin, but as this latter substance is difficult to manufacture, it is better to first make the glycerin ester of the acid in question and then nitrate with sulphuric and nitric acids.

The ester groups may be detected and estimated by the usual methods.

Dinitromonochlorhydrin, $C_3H_5Cl(NO_3)_2$, is made by nitrating monochlorhydrin (Roewer, *Zeits. Schiess-Sprengstoffwesen*, 1909, **1,** 229). It is a yellowish mobile liquid of slightly aromatic odour. It is soluble in organic solvents, such as ether, alcohol, acetone, and chloroform, but insoluble in water and acids. The sp. gr. is 1.54 at 15°. Under atmospheric pressure it boils at 190° to 193° with some decomposition. Under 15 mm. it distils at 121 to 123°, giving an almost colourless distillate. It is not hygroscopic, and does not freeze at −25 to −30°. It dissolves collodion cotton very readily. An addition of 20% to nitroglycerin produces an explosive which is practically unfreezable. The mixture of nitroglycerin and dinitromonochlorhydrin is best made by nitrating a mixture of glycerin and chlorhydrin.

NITRATES OF POLYMERISED GLYCERIN.

It has been found by Will that if glycerol is heated at 290° for 7 or 8 hours under a condenser, which will allow water vapor to escape but condense any glycerol vapor and return it to the vessel, the material is

partly converted into "diglycerol" $C_3H_5(OH)_2.O.C_3H_5(OH)_2$, and if this is then nitrated in the usual way a nitroglycerin is obtained containing 20 to 25% of tetranitro-diglycerin. This mixture resembles ordinary nitroglycerin in all respects except that it freezes less readily (*Zeits. Schiess-Sprengstoffwesen*, 1906, **I,** 231).

Glycerol can also be polymerised by the action of hydrochloric acid.

These derivatives of nitroglycerin have not been used at all extensively hitherto. Before they are manufactured on a large scale it is essential that prolonged trials be carried out to ascertain if they possess a sufficient degree of chemical stability.

PICRIC ACID.

This substance is the final product of the action of nitric acid on a large number of substances containing a benzene nucleus just as oxalic acid is the result of the oxidation of many bodies of the fatty series. Picric acid is obtainable from indigo, aloes, gum-resins, wool, silk, etc., but the common idea that the yellow colour produced by nitric acid on animal tissues, such as skin, wool, etc., is due to the production of picric acid is erroneous: it is due to the formation of xanthoproteic acid.

Picric acid was formerly prepared by the direct action of nitric acid on phenol, but is now made by first dissolving the phenol in strong sulphuric acid and then acting on the resulting phenolsulphonic acid with excess of nitric acid. Mono- and dinitro-phenol may result if the action is not carried far enough. Picric acid separates from the acid mixture as an oily liquid, which solidifies on cooling. It is purified by recrystallisation from water.

Picric acid may also be prepared by acting on phenoltrisulphonic acid with sodium nitrate.

Picric acid forms pale yellow, crystalline needles or scales, of an intensely bitter taste and sp. gr. 1.777. The pure acid melts at 122° and the common at a lower temperature to a brownish-yellow oil, which at a higher temperature partially sublimes, and boils with formation of yellow, bitter, suffocating vapours. The lower m. p. of impure picric acid is probably due to an admixture of dinitrophenols or of a nitrocresol. Hence the m. p. of picric acid is a test of its purity.

When strongly heated, picric acid burns rapidly with formation of

an intensely black smoke. It does not explode when heated under ordinary conditions, but it can be made to explode by allowing it to fall into a tube heated to a red heat. The disastrous explosion which occurred at the factory of Griessheim-Elektron showed that it could detonate without the use of a detonator, and the subsequent catastrophe at Woolwich Arsenal confirmed this.

Picric acid can be detonated by a blow, a charge of 5 grains of mercuric fulminate sufficing to determine the explosion. The detonation of one charge will cause the detonation of neighboring quantities, and even wet picric acid can be exploded by this means. Metallic picrates, and notably lead picrate, or even an imperfect mixture of picric acid with lead oxide or nitrate, will detonate violently when heated, and the explosion will induce the detonation of neighboring quantities of picric acid or picrates. This property of the picrates has led to their employment in several detonating and explosive mixtures. Disastrous fires and explosions have occurred through the negligent handling and storage of picric acid.

Picric acid is soluble in about 15 parts of boiling water, but it requires 26 parts at 76° and 86 at 15°. The solution is intensely bitter, bright yellow, and reddens litmus. In a stratum 1 inch in depth, the yellow colour of a solution of 1 part of picric acid in 30,000 of water is distinctly visible. The yellow colour of picric acid solutions is intensified by neutralisation with an alkali. A cold aqueous solution of picric acid gives a copious precipitate on adding hydrochloric acid.

Picric acid is readily soluble in alcohol, ether, chloroform, benzene, petroleum spirit, etc.; the last four solutions being colourless or nearly so. Such of the above solvents as are not miscible with water remove picric acid more or less perfectly from its aqueous solution, or that of a picrate which has been freely acidulated with sulphuric acid. Ether is preferable to chloroform for this purpose. A solution of picric acid in ether gives up the greater part of its colour to water, but on adding sulphuric acid or, still better, hydrochloric acid, the condition is reversed, the picric acid going chiefly into the ether.

All the above solutions of picric acid, including that in water, dye silk, wool, skin, and other nitrogenous organic matters yellow with a slightly greenish shade. The stain is not removable by water, but soap or alkali partly destroys it. Animal charcoal absorbs a large quantity of picric acid from its aqueous solution. Picric acid is used as a dye for silk and wool, but is employed to modify the

shades of other colours rather than as an unmixed dye. Thus with methyl-green it gives yellow-green, with indigo-carmine or aniline-blue a deep green, and with magenta a very fast scarlet. Since the introduction of the yellow azo-dyes the employment of picric acid has decreased.

It is now used extensively as a filler for shells, and has been given various names in different countries when used in this way. The French call it melinite, the English lyddite, and the Japanese shimosite. Lyddite consists simply of picric acid, which is melted and poured into the shell. A cylindrical space is left in the centre, into which is inserted an exploder containing "picrate powder," a mixture of ammonium picrate and potassium nitrate, and this in turn is exploded by means of a detonator.

There is some objection to the use of picric acid in consequence of its liability to form very sensitive picrates with nearly all metals except tin. There is consequently considerable probability that will be displaced as a filler by some other aromatic nitro-derivatives not so strongly acid in character.

Picric acid forms a series of well-defined crystallizable salts and also combines with organic bases. With certain hydrocarbons it forms characteristic crystalline compounds of the formula $XC_6H_8(NO_2)_3O$, in which X represents a molecule of the hydrocarbon. The reaction has been utilised for the purpose of distinguishing hydrocarbons, especially those of the anthracene group, and the formation of the naphthalene and acridine picrates has been suggested as a means of identifying picric acid.

Detection and Estimation of Picric Acid.—The yellow colour and extremely bitter taste of the aqueous solution of picric acid, the deepening of the yellow colour on adding excess of alkali, and the power possessed by the solution of the free acid by dyeing immersed wool or silk yellow are themselves important indications of its presence. In the presence of other colouring or interfering bodies, the picric acid may be extracted from the aqueous solution by agitation with ether or amyl alcohol, after strongly acidulating with sulphuric acid. The picric acid may then be recovered by evaporating the ethereal solution or agitating it with solution of sodium hydroxide, when it will pass into the alkaline liquid. The extraction of picric acid from an acidulated solution by ether, benzene, or amyl alcohol may be made quantitative.

Picric acid may be titrated with ease and accuracy by standard

alkali and phenolphthalein (P. Kay, *J. Soc. Dyers, etc.*, **4,** 84). The process is applicable to the ethereal or benzene solution of picric acid if this be first diluted with alcohol.

An aqueous solution of picric acid is not precipitated on adding neutral lead acetate, but basic or ammoniacal lead acetate gives a bright yellow precipitate even with very dilute solutions of picric acid.[1]

Picric acid is not precipitated from its aqueous solution by copper sulphate; but the ammonio-sulphate produces a bright green precipitate, which is insoluble in ammonia and is decomposed by washing with water. A solution containing 1-10,000 of picric acid gives a distinct precipitate with ammonia-copper sulphate in 24 hours.

If a solution of picric acid be treated with zinc and dilute sulphuric acid, a turbid yellowish-red solution is obtained, which, when poured off from the excess of zinc and mixed with alcohol, develops a green colour, changing through blue to a violet.

By the action of tin and hydrochloric acid in a warm solution, picric acid is completely reduced to the colourless hydrochloride of triamidophenol, $C_6H_2(NH_2)_3.OH$. In alkaline solutions, the reduction does not proceed so far, picramic acid, $C_6H_2(NO_2)_2(NH_2).OH$, being the product. This reaction occurs most readily by passing hydrogen sulphide through a saturated alcoholic solution of picric acid neutralised with ammonia. Dark red crystals of ammonium picramate are deposited, from which the free acid may be prepared by dissolving in hot water and adding acetic acid. Picramic acid forms beautiful red needles, almost insoluble in water even when hot, but soluble in alcohol and ether. It dyes silk and wool brown.

When a solution of picric acid is boiled with a strong solution of potassium cyanide, a deep red liquid is produced, owing to the formation of potassium iso-purpurate, a body which crystallises in small reddish-brown plates with a beetle-green lustre, and is slightly soluble in cold, but more readily in hot water. By reaction with ammonium chloride, it gives ammonium iso-purpurate, $NH_4,C_8H_4N_5O_6$, or artificial *murexide*, which in a slightly acid bath dyes silk and wool brown-red. It was formerly employed under the name of "grenat soluble," but is not now used. On adding barium chloride to a solution of either of the above salts a vermilion-red precipitate is formed, consisting of

[1] If the precipitate is decomposed by dilute sulphuric acid, and the filtered solution rendered ammoniacal and evaporated to dryness, a residue is obtained which gives a deep brown colour on heating with potassium cyanide. This behaviour distinguishes picric acid from quercitron and such other vegetable yellow colouring matters as are precipitated by basic lead acetate.

barium iso-purpurate.   True iso-purpuric acid is very unstable and is
practically unknown.

Aniline yellow of commerce dissolves in water with redder colour
than picric acid.   It is not altered by potassium cyanide, but is turned
purple by hydrochloric acid.

Picric acid, when boiled with a strong solution of calcium hypo-
chlorite (bleaching powder), gives off pungent and tear-exciting vapours
of chloropicrin.

Picric acid forms highly insoluble compounds with many of the
vegetable alkaloids, and the insolubility of the cinchonine salt has
been employed for the determination of picric acid.   A solution of
cinchonine sulphate acidulated with sulphuric acid is added to the
picric acid solution.   The precipitate of cinchonine picrate, $C_{20}H_{24}$-
$N_2O(C_6H_3N_3O_7)_2$, is washed with cold water, rinsed off the filter into
a porcelain crucible or dish, the water evaporated on the water-bath,
and the residual salt weighed.   The yellow, intensely bitter alkaloid
berberine, is said to precipitate picric acid so perfectly that, on mixing
the picric and alkaloidal solutions in equivalent proportions and
filtering, the filtrate is colourless and free from bitterness.

The *cinchona* alkaloids, the opium bases (except morphine and
pseudo-morphine), the *strychnos* alkaloids, veratrine, berberine, and
some others, are completely precipitated by picric acid from their
dilute solutions, if acidulated by sulphuric acid, but not in presence of
free hydrochloric acid.   Caffeine and the glucosides are not precipi-
tated by picric acid.

Some of the colour bases from coal-tar form extremely insoluble
picrates, and have been employed by Kay and Appleyard (*J. Soc.
Dyers, etc.*, **4,** 83) for the estimate of picric acid.   For this pur-
pose they prefer the dye known as night-blue, which is the tetra-
methyltolyltriamido-diphenyl-naphthyl-carbinol hydrochloride.   The
commercial product is purified by precipitating the aqueous solution
with ammonia, washing well with water, and drying the precipitate
over strong sulphuric acid.   A weighed quantity of the base is dis-
solved in acetic acid and the solution diluted to a known volume.   For
the titration, a known volume of the night-blue solution is measured
into a flask, and the solution of picric acid run in from a burette.   486
parts of the night-blue base correspond to 229 of picric acid, the picrate,
which forms a dark precipitate, having the formula $C_{34}H_{36}N_3$.
$C_6H_2(NO_2)_3OH$.   The picric acid solution should contain 1 grm. of

the sample per litre, and by comparing the volume of the solution used with the measure of a solution of pure picric acid employed in a parallel experiment, the proportion of impurity may be readily ascertained. The end of the reaction is very sharply defined, as by tilting the flask on one side, so that a portion of the clear liquid may run into the neck, it is easy to observe whether the solution retains any blue colour. A very slight excess of picric acid is sufficient to produce a marked yellow tint. If desired, a portion of the liquid may be filtered for the better observation of its colour, but this is rarely necessary.

Crystal violet, the hydrochloride of hexamethyl-rosaniline, may be substituted for the night-blue in the above process. 443.5 parts of this colouring matter, when dissolved in water, react with 229 parts of pure picric acid to form a picrate of the formula $C_{25}H_{31}N_3.C_6H_2(NO_2)_3OH$. This precipitate is flocculent, and when in suspension exhibits such a powerful coppery reflex that the liquid containing it appears brown by reflected light.

The picrates of rosaniline, safranine, methyl-violet, methylene-blue, and malachite-green are also nearly insoluble in water, but not sufficiently so to render the bases desirable substitutes for night-blue or crystal-violet in the above process.

Of the compounds of picric acid with solid hydrocarbons, that with naphthalene, $C_{10}H_8 + C_6H_3(NO_2)_3O$, is almost the only one precipitated when the cold alcohol solution of the hydrocarbon is mixed with a cold alcoholic solution of picric acid. It forms stellate groups of golden-yellow needles, melting at 149°. The formation of naphthalene picrate may be employed to distinguish picric acid from similar nitro-compounds.

Acridine has been suggested by Anschütz (*Jour. Soc. Chem. Ind.*, 1884, **3**, 234) as a suitable reagent for the determination of picric acid, the hydrochloride being used as a precipitant for metallic picrates and a solution of the free base in benzene for the picric acid compounds of hydrocarbons.

The nitrogen may be estimated in picric acid by the Kjeldahl or Dumas method. Picric acid and picrates may therefore be estimated by this means. In the Lunge nitrometer they evolve no gas.

Picric acid has been used occasionally to communicate bitterness to *beer*, less than 1 grain per Imperial gallon being amply sufficient for this purpose. The most delicate and satisfactory method for the detection of picric acid in beer is to concentrate 100 c.c. by evaporation

to about 30 c.c.; then acidify with sulphuric acid and agitate with ether or petroleum spirit. The ethereal solution is separated and evaporated. The residue is dissolved in hot water and the solution heated on the water-bath for some time with a small quantity of clean white wool, which in presence of picric acid will acquire a yellow colour. 1 part of picric acid in 100,000 of beer may be detected by this method. Amyl alcohol has been proposed as a substitute for ether but is not so satisfactory. By first precipitating the beer with neutral lead acetate and filtering, the colouring matter of the beer may be removed and the indications made more delicate. As a confirmation, the dye may be removed from the wool by warming it with dilute ammonia, filtering, and evaporating the filtrate to a very small bulk on the water-bath. On then adding a few drops of potassium cyanide solution and heating, a distinct red-brown will be produced in presence of picric acid;[1] or the ammoniacal extract may be treated with zinc and hydrochloric acid and the solution diluted with alcohol as described on page 579.

It is evident that the method just described is applicable to the detection of picric acid on animal fibres, such as *silk* or *wool*.

Commercial Picric Acid.—The picric acid of commerce is generally crystallised. Though now of much better quality than formerly, it is still liable to contain impurities, and occasionally is intentionally adulterated. Thus sodium sulphate is sometimes added before crystallisation, and oxalic acid and sugar are said to be occasionally met with.

The m. p. of pure picric acid is 122°, and the best commercial samples do not melt below 121°. A lower m. p. indicates the presence of *dinitrophenol* or a *nitrocresol*. The first impurity is due to imperfect nitrification and the latter to the employment of a phenol of low m. p. (therefore containing cresol) for the manufacture.

General impurities and adulterations may be detected and determined by treating 2 grm. of the finely-powdered sample with 50 c.c. of ether. The picric acid dissolves, while any picrates, nitrates, oxalic acid, boric acid, sodium sulphate, alum, sugar, etc., will be left insoluble, and, after removal of the ethereal liquid, may be readily identified and determined. For the detection and estimation of *water* and *oxalic acid*, 50 c.c. of warm benzene may be advantageously substituted for

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[1] A rough colorimetric determination of the amount of picric acid present may be based on the depth of colour produced.

the ether. Sugar and boric acid may be separated from the other impurities by treating the residue insoluble in ether or benzene with rectified spirit. If *boric acid* is present the alcoholic solution will burn with a green flame. *Sugar* may also be sought for by neutralising the aqueous solution of the sample by sodium carbonate, evaporating to dryness, and extracting with proof-spirit, which will dissolve any sugar and leave the sodium picrate insoluble.

Sulphuric, hydrochloric, and oxalic acids, and their salts, may be detected by adding solutions of barium, silver, and calcium, respectively, to the warm, filtered, aqueous solution of the sample. o.2% of SO_3, as estimated by precipitation as barium sulphate, is the maximum proportion allowed by the French Government in picric acid intended for the manufacture of mélinite. *Free sulphuric acid* might be detected by dissolving the sample in warm benzene, agitating the solution with warm water, removing the benzene layer, and again agitating the aqueous liquid with benzene, till all yellow colour is removed. On then titrating the aqueous liquid with standard alkali, the volume required for neutralisation will correspond to the free sulphuric or other mineral acid of the sample.

It is possible that commercial picric acid occasionally contains a *nitrophenolsulphonic acid*. Such an impurity would be indicated by the presence of sulphates in the residue obtained on igniting with a large excess of alkali. (See *Analyst*, 1888, **13**, 43.)

If the process of nitrification has been imperfect, the resultant picric acid will be liable to contain *dinitrophenol* (see above). This impurity lowers the m. p. of the sample. The calcium salt is less soluble than calcium picrate, and if present in sufficient quantity may be separated from the latter by fractional crystallisation or by precipitating the hot saturated aqueous solution of the sample with excess of lime-water.

A method of estimating small proportions of dinitrophenol in picric acid is by treating the aqueous solution of the sample with bromine, as proposed by Allen (*J. Soc. Dyers, etc.,* **4**, 84). With dinitrophenol the following reaction occurs: $C_6H_3(NO_2)_2OH + Br_2 = HBr + C_6H_2Br(NO_2)_2OH$. With picric acid, bromine reacts as follows: $C_6H_2(NO_2)_3OH + Br_2 = HBr + HNO_3 + C_6H_2Br(NO_2)_2OH$. In each case two atoms of bromine enter into the reaction, with formation of a bromodinitrophenol (the same in each case) and one molecule of hydrobromic acid. But in the case of picric acid, nitric acid is

formed in addition, and hence the acidity of the liquid at the end of the reaction would be greater the larger the proportion of picric acid present. If the bromodinitrophenol and excess of bromine[1] were removed by agitation with ether or similar solvent, the acidity of the aqueous liquid could be ascertained with great accuracy by titration with standard alkali.

The reaction between bromine and dinitrophenol occurs promptly, but in the case of picric acid it was gradual. In 12 hours it is complete, but in the course of a few minutes almost nothing. This fact enables the reaction with bromine to be utilised for the direct estimation of the dinitrophenol, instead of for its indirect estimation (by estimating the picric acid), as when the acidity is ascertained. The following method of operating was found by the author to be the most satisfactory: 1 grm. of the sample of picric acid is dissolved in about 100 c.c. of warm water. A saturated solution of bromine in water is diluted with twice its measure of water in a large tapped and stoppered separator, and from this run into a burette. From this burette, a definite volume of the bromine solution, which is approximately of 1% strength, is run into a flask and an equal measure into another similar flask, both of which are immediately closed. The picric acid solution is then poured into one of the flasks, the last drops rinsed in without delay, and then an excess of a solution of potassium iodide at once added to the contents of both flasks. The liberated iodine is then determined by titration with a decinormal solution of sodium thiosulphate (hyposulphite) in the usual way.[2] From the difference in the volume of the solution required in the 2 experiments the amount of bromine which has reacted with the dinitrophenol is easily found. *Dinitrophenol* reacts with 86.96% of bromine, taking up 43.48%. *Mononitrophenol*, if present, which is improbable, would react with 230.2% of bromine, taking up 115.1% to form the compound C_6H_2-$Br_2(NO_2).OH$. Allen has verified these reactions by experiments on specially prepared mono- and dinitrophenol. When the process is applied to commercial picric acid the results are liable to be somewhat in excess of the truth, owing to slight action of the bromine on the picric acid itself.

Commercial picric acid often contains red particles. These have

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[1] If preferred, before extracting with ether the excess of bromine may be got rid of by adding potassium iodide and then sufficient sodium thiosulphate to react with the iodine liberated.

[2] Allen found iodine to be wholly without action on solutions of either mono-, di-, or trinitrophenol.

been attributed to the presence of dinitrophenol, but from an obser-
vation of T. Whitaker (*J. Soc. Dyers*, **4,** 87) it is not improbable
that they consist of a *nitrosophenol*.

A method for the detection of picric acid is given by A. Ryniska
(*Zeit. anal. Chem.*, 1897, 813). The substance is macerated for
several hours with water, acidified with sulphuric acid, then mixed
with three volumes of 95% alcohol, and digested for 24 hours at
50 to 60°. After filtration and evaporation of the alcohol, any fat is
removed by shaking with light petroleum, and the liquid is then
acidified with hydrochloric acid and shaken repeatedly with ether.
Urine, which in cases of poisoning with picric acid is always coloured
reddish-brown by the presence of picramic acid, may be extracted
with ether after simply acidifying. The residue obtained by evaporat-
ing the ether is then tested for picric acid by (1) the isopurpuric
reaction (blood-red colour on warming with potassium cyanide and
sodium hydroxide); (2) the picramic acid reaction (blood-red colour
on heating with sodium hydroxide and grape-sugar), or, better (3)
hydroxide and sodium sulphide; (4) ammoniacal copper solution
(yellow-green crystals which polarise light); and (5) by dyeing white
wool. The limit of sensitiveness of the 5 reactions is 1:5000, 1:7000,
1:12500, 1:80000, and 1:110000 respectively. Reactions (2) and (5) are
less sensitive in presence of fats and other substances (see also Vol. 5).

Metallic Picrates.—As a rule, the picrates are possessed of but
little solubility. They are yellow in colour and crystallise well. Many
of them explode violently when heated or struck, and hence they are
employed in admixture with metallic chlorates or nitrates as detonating
charges for shells.

Potassium picrate forms long yellow needles when a strong
solution of picric acid is neutralised by potassium carbonate or hy-
droxide. The salt requires 288 of cold or 14 parts of boiling water for
solution, and in alcohol is nearly insoluble. The aqueous solution is
much more strongly coloured than a solution of free picric acid of
corresponding strength. When heated, potassium picrate becomes
red and explodes like gunpowder, and when strongly struck it detonates
violently.

Sodium picrate is readily soluble in pure water, but nearly in-
soluble in solution of sodium carbonate or hydroxide.

Ammonium picrate crystallises in rhombic scales which are some-
what more soluble than the potassium salt. It is used in conjunction

with potassium nitrate as a detonating charge for picric acid (lyddite).

Lead picrate crystallises in brown needles soluble in 119 parts of cold water. In admixture with nitre it is employed as an explosive. A rough mixture of picric acid with red lead or litharge detonates violently when strongly struck.

MERCURIC FULMINATE.

This is made by dissolving mercury in nitric acid (sp. gr. 1.4) and pouring into warm alcohol. An energetic reaction takes place. On cooling, crystals of mercuric fulminate separate; they are filtered off and washed until neutral. The product may be purified by recrystallisation from water. Its sp. gr. is 4.42. 1000 c.c. of water dissolves 0.71 grm. at 12° and 1.74 grm. at 49°.

Mercuric fulminate is extremely sensitive to friction and shock and explodes with tremendous speed. Hence its use as a detonator for igniting other explosives, which are less sensitive. It is always stored wet, and in fact under water until required for use. The very greatest care has to be taken in drying, weighing, and mixing it. It is frequently used by itself in caps and detonators, but many explosives are better ignited by compositions containing other substances mixed with the fulminate to reduce its violence. The principal of these substances are potassium chlorate, antimonous sulphide, powdered sulphur, charcoal, and potassium nitrate.

Silver fulminate may be made in the same manner as the mercury compound. It is even more sensitive than the latter, and is practically never used except for making caps for toy pistols.

For methods of examining caps, physical as well as chemical, see Brownsdon (*J. Soc. Chem. Ind.*, 1905, **24**, 381). The chemical methods are as follows:

Analytical Examination of Caps.—The quantities most easily and accurately determined are: 1. weight of charge; 2. weight of fulminate, and 3. weight of antimonous sulphide (stibnite). From the figures so obtained the percentage of fulminate and stibnite per cap can be ascertained, and that of chlorate and other ingredients indirectly by difference. In the estimation of such small quantities of fulminate and stibnite as are contained in a cap, special methods must of necessity be used. By the use of the methods given in detail below, the weight of fulminate and stibnite are obtained easily within 20

minutes of commencing the analysis. The methods are volumetric, the only weighings required being those from which the weight of charge is obtained.

Weight of Charge.—This is best ascertained by difference, first weighing the cap, and afterward the empty shell plus tin foil, after extracting the composition. The difference gives the weight of the composition plus varnish. The weight of varnish is small and may be ascertained in a number of caps, the mean being deducted from the above weight found. If comparative and not absolute figures are required, it may be neglected, since it does not affect the weight of fulminate or stibnite. The extraction of the composition is most conveniently and completely done over a porcelain dish of about 200 c.c. capacity by squeezing with pliers and removing the loosened foil and broken composition by means of a pointed wooden chip. Composition adhering to the shell or foil is loosened by alcohol and washed into the dish by means of alcohol from a small wash-bottle. The shell and foil are put on one side and subsequently weighed when dry. It is convenient to extract the composition at the same time from a number of caps.

Fulminate.—The composition in the dish is broken down quite fine with a flat-headed glass rod, and the alcohol evaporated on a water-bath till the residue is moist, but not quite dry; 25 c.c. of water are then added and the composition stirred from the bottom. After the addition of 0.5 grm. of pure sodium thiosulphate, the contents of the dish are stirred for 2 1/2 minutes. One drop of methyl-orange is then added and the solution titrated with N/20 sulphuric acid. The acid is standardised against weighings of 0.05 to 0.1 grm. of pure fulminate, to which are added 25 c.c. of water and then 0.5 grm. of thiosulphate. This is stirred for 2 1/2 minutes and then titrated with N/20 sulphuric acid. The small amount of antimonous sulphide present does not interfere with the recognition of the end-point. After titration the solution is filtered through a small filter-paper, which retains the antimony sulphide.

Antimonous Sulphide.—The filter-paper containing the antimonous sulphide is well washed and then transferred to a large test-tube. 5 c.c. of strong hydrochloric acid are added and the contents of the tube boiled gently for a few seconds until the sulphide is dissolved and all the hydrogen sulphide has been driven off or decomposed. 3 c.c. of a saturated solution of tartaric acid are then added and the contents of the tube washed into a conical flask of about 250 c.c. capacity. The

solution is then nearly neutralised with sodium carbonate, excess of sodium hydrogen carbonate is added, and after the introduction of some starch solution the liquid is titrated with N/20 iodine solution. This method for small quantities of antimonous sulphide is both quick and accurate: the error does not exceed 0.0003 grm.

There are two forms of commercial mercuric fulminate, "white" and "grey." To obtain the former small amounts hydrochloric acid and metallic copper (about 1:1,000) are added to the nitric acid solution of mercury in the manufacture of the fulminate. The white is not necessarily purer than the grey; apparently the blue tint of the copper salts neutralises the yellowish tint of the fulminate and a fine precipitate of cuprous and mercurous chlorides helps to whiten the product.

Various impurities are liable to be formed in the process of manufacture and the amount of these may be considerable, if great care be not exercised in measuring out the ingredients, adjusting the temperature, and attending to the other details.

Mercuric fulminate should be white or light grey in colour with a slight tinge of yellow. It should dissolve readily and completely or almost completely in ammonia and in concentrated hydrochloric acid and in potassium cyanide solution. The exact nature of the compounds that are insoluble or difficultly soluble in these reagents is not known and they are probably different in different cases. They include mercurous salts, mercuric fulminate, and metallic mercury. Metallic mercury is said to be specially injurious to fulminate because it amalgamates the copper caps and thus leads to the formation of cupric fulminate. To test for metallic mercury, treat the fulminate repeatedly with strong hydrochloric acid until any mercurous chloride, which forms, has been dissolved, wash by decantation with water and examine the residue under the microscope for beads of mercury. Another method is to rub the fulminate in the wet state on a gold plate with a gold rod. If any white specks of gold amalgam are formed it shows the presence of metallic mercury. It is stated by Solonina (*Zeits. Schiess-Sprengstoffwesen*, 1910, **5,** 41 and 61) that white fulminate never contains free mercury. Other impurities liable to be present are mercurous compounds and oxalates. The former yield mercurous chloride when treated with hydrochloric acid and only dissolve with difficulty in excess of the hot reagent. Pure fulminate dissolves readily and completely in hydrochloric acid.

The oxalate may be estimated as follows: The fulminate is dissolved in ammonia solution, ammonium sulphide is added to precipitate the mercury, the solution is filtered, washed, and to the filtrate ammonium chloride and calcium chloride solutions are added. After standing overnight the calcium oxalate is filtered off and estimated by one of the usual methods.

Mercuric fulminate when recrystallised from hot water is said to contain half a molecule of water of crystallisation, but it is doubtful whether the product has a high degree of purity, because hot water converts some of the fulminate into fulminurate and mercuric oxide. For the purification of fulminate, it is better to dissolve it in potassium cyanide solution and reprecipitate with dilute nitric acid. This is the method adopted by Brownsdon to obtain a pure product for standardising the sulphuric acid:

About 0.8 part by weight of potassium cyanide are dissolved in ten of water and then one part of fulminate is gradually added with constant stirring. When solution is complete the insoluble residue is filtered off and dilute nitric acid is added to the filtrate until no further precipitate is formed. The white powder is allowed to settle, washed several times by decantation, and then on the filter with distilled water until it is no longer acid. It is then pressed between filter-paper and dried first in the air and then in a desiccator and kept in a dark place.

For the purification of mercuric fulminate on a commercial scale, Solonina recommends that it be dissolved in pyridine and reprecipitated with water. It is not customary, however, to purify mercuric fulminate except by washing with water until neutral.

Other substances that are frequently used together with fulminate to compose the mixtures used for filling caps and igniters are mealed gunpowder, sulphur, potassium nitrate, potassium chlorate, ground glass, and antimonous sulphide.

Sometimes mixtures are used containing no fulminate. The surface is generally covered with shellac varnish. Detonators for firing high explosives are usually filled with fulminate alone or mixed with a small proportion of potassium chlorate.

SOLVENTS.

In the manufacture of propulsive explosives the nitrocellulose is gelatinised by means of a suitable solvent. For nitrocellulose con-

taining 13% of nitrogen acetone is mostly employed and this is the solvent used in the manufacture of cordite (see Marshall, *J. Soc. Chem. Ind.*, 1904, **23,** 645). Amyl and ethyl acetates have, however, been used for some powders; they are easily detected by their characteristic odours. A mixture of ether and alcohol is usually used for gelatinising "soluble" nitrocelluloses.

Other mixtures, such as acetone and ether, are used in other cases. In the French military powders, amyl alcohol is added; it prevents the nitrocellulose becoming degelatinised and appears not only to maintain the ballistics of the explosive, but also the chemical stability to some extent.

The solvent used for gelatinising as explosive can usually be detected by the odour when warmed in the ground state in a test-tube, as is done in carrying out the heat test (see below). An old powder, for which ether-alcohol has been used, will give the characteristic sweet smell of ethyl nitrate. Old cordite, on the other hand, has an acid smell probably due to acetic and formic acids formed from the acetone. The quantity of solvent remaining in an explosive is determined as described below under "Moisture and Volatile Matter."

WOOD MEAL.

Wood meal is a constituent of carbonite and many other high explosives. It serves the double purpose of absorbing the nitroglycerin and reducing the temperature of explosion. It should be free from acid and foreign substances, especially particles of metal, and should not contain much resin. The moisture should not exceed about 5%. It should absorb nitroglycerin readily.

Other Materials.

Although the substances dealt with above are the most important constituents of modern explosives, there are many others that are used, and in fact there are few commercial materials that have not at any rate been proposed at some time or other. All highly nitrated nitro-derivatives and organic nitrates are more or less explosive, and the greater the number of nitro-groups the more explosive they are; trinitrotoluene and the nitrocresols are very usual constituents of high explosives. The lower nitro-derivatives, such as mononitrobenzene,

are also frequently employed in conjunction with substances that contain an excess of oxygen. Among the secondary constituents of composite explosives there are many that contain no oxygen, such as mineral jelly (vaseline), wood pulp, and starch. There are also the solvents used for gelatinising the nitrocellulose: acetone, alcohol, ether, and amyl acetate. These substances are dealt with in other sections.

Since the introduction of Franke's process for utilising the nitrogen of the atmosphere, it has been proposed to use cyanogen derivatives, such as dicyan diamide, as constituents of explosives. It is claimed that they increase the stability and the gas evolution, but diminish the temperature of the products of explosion.

Other organic substances that may be found in various explosives are castor oil, starch, resin, glue, dextrin flour, paraffin, and naphthalene. These are not explosives and are employed in conjunction with organic or inorganic materials containing an excess of oxygen. It should be borne in mind that the competition in the explosives industry is keen, prices obtainable are not high, and therefore rare and expensive substances cannot be used and need not be sought for.

The inorganic materials used include the potassium, sodium, and ammonium nitrates, chlorates, and perchlorates, calcium and sodium carbonates, barium nitrate, aluminium, kieselguhr, and several sulphates and chlorides. Ammonium oxalate is present in many high explosives.

In France and Germany attempts have been made to increase the stability of explosives by adding small quantities of urea, aniline, diphenylamine and other substances which will combine with nitrogen oxides, but these additions do not appear to produce the desired effect.

COMPOSITE EXPLOSIVES.

Nitrocotton is present in most modern explosives. Many contain more than 50% and some consist almost entirely of it. Nitroglycerin is also a very frequent constituent. These substances are detected and estimated by the methods given above.

Moisture and Volatile Matter.—All explosives that have been wholly or partly gelatinised retain more or less of the organic solvent used. In the case of the larger sizes of "cordite M. D." it amounts frequently to more than 1%, and nitrocellulose powders, in which there

is no nitroglycerin, generally contain several %, which it is impracticable to drive off in the drying stoves, as it is retained by the colloid with great obstinacy.

In the case of explosives not containing nitroglycerin, camphor, or any other constituent that it is slightly volatile, the material is ground and sifted, and 2 grm. are weighed out onto a watch-glass and dried in an oven at a suitable temperature to constant weight. As a rule, it is not advisable to use for this purpose material that has been ground more finely than is laid down in the directions for the heat test, because the very fine material loses a considerable proportion of its volatile matter during the grinding, sifting, and weighing. The temperature of the oven is usually somewhere between 65 and 100°. Explosives that are thoroughly stable will withstand the latter temperature for several hours without undergoing a sufficient amount of decomposition to affect the results. In the case of unstable materials a lower temperature must be employed, however, and in extreme cases the drying should be carried out at the ordinary temperature in a vacuum desiccator over sulphuric acid.

Moisture in Nitroglycerin Explosives. (See Marshall, *J. Soc. Chem. Ind.*, 1904, **23**, 154).—The difficulty to be overcome in this instance is the fact that nitroglycerin itself is slightly volatile. But investigations carried out at the Royal Gunpowder Factory, Waltham Abbey, showed that the difficulty could be overcome by the use of a special apparatus, consisting of an aluminium dish covered with a glass cone, so as to leave only a very slight space between them for the escape of the vapour of water and organic solvent.

The apparatus is warmed and allowed to stand for 1/2 hour in a desiccator to acquire constant weight. Then 5 grm. of the sample are placed in the aluminium dish, the glass cone is put over it, and the whole is weighed. The apparatus is then stood upon a metal plate heated below by boiling water or steam: the top of an ordinary boiling-water oven is suitable. Here it is allowed to stand until the weight is practically constant. In the case of "cordite, mark I", or ballistite, or blasting gelatine an hour is sufficient; "cordite M. D." requires 2 hours. The apparatus is then removed to the desiccator, allowed to stand for 1/2 hour and weighed. The loss of weight is the amount of moisture (volatile matter) in the explosive taken. Any nitroglycerin that is driven off from the powder by the heat is condensed on the glass cone; the loss of nitroglycerin from the apparatus is less than 0.01%.

The results are very consistent. The material should be ground and sifted in the same manner as is laid down in the instructions for the heat test.

For the estimation of the water only in substances which contain also acetone and other volatile compounds Dupré recommends the use of calcium carbide (*Analyst*, 1906, **31**, 213). The ground material is put into a tube 1 cm. wide and 10 cm. long and covered first with a layer of dry sand and then with a layer of carbide 5 cm. high. The tube is connected to a nitrometer filled with saturated brine, and heated in a water-bath to 100°. The moisture reacts with the carbide producing acetylene. Taking into account the water taken up by the lime 1 c.c. acetylene corresponds to 0.001725 grm. water.

Other Constituents.—A further portion of 2 grm. is weighed out into a corrugated hardened filter-paper, and extracted with ether (sp. gr. 0.720) in a Soxhlet. The extract may contain nitroglycerin, resin, camphor, sulphur, mineral jelly (vaseline), or paraffin. Mineral jelly and paraffin, being insoluble in 80% methyl alcohol, can be separated quantitatively from the nitroglycerin, etc., by the use of this solvent. After distilling off the ether, a mixture 80 parts by volume of absolute methyl alcohol and 20 of water is added to the material in the extraction flask, which is then heated on a boiling water-bath. The liquid is allowed to settle for a minute or two and then is decanted through a small filter or directly into a clean beaker. After repeating this operation about 4 times, the mineral jelly is quite free from nitroglycerin. After the first washing it is advisable to heat the flask again before adding more alcohol, in order to cause the mineral jelly to adhere to the glass. If any globules of the mineral jelly get into the filter or beaker, they must be washed free from nitroglycerin, and then transferred back into the extraction flask, if necessary with the aid of a little ether. After drying in a steam-oven the mineral jelly may be weighed in the extraction flask.

Cordite and cordite MD have the following composition:

	Nitroglycerin	Guncotton	Mineral jelly	Moisture.
Cordite........	58%	37%	5%	0.25 to 0.5%
Cordite MD....	30%	65%	5%	0.4 to 1.0%

It will be seen that the methods already given will suffice for the complete analysis of these explosives. The ash may be ascertained as described above under Nitrocellulose.

In the case of an explosive of unknown composition the contents of the filter-paper may now, after weighing, be further extracted with water, which will dissolve any nitrates, chlorates or soluble carbonates, or other salts or materials soluble in water. The matter dissolved out is analysed by the usual methods. The contents of the filter-paper can then be further extracted with benzene, chloroform, etc. The final residue will probably consist entirely of nitrocellulose, which after weighing can be examined as described above for percentage of nitrogen, solubility in ether-alcohol, etc. In the case of an unknown explosive it is desirable to examine the matter insoluble in acetone. Blasting explosives frequently contain wood meal, infusorial earth, and other similar organic and inorganic materials: these will be found in the matter insoluble in acetone.

STABILITY TESTS.

Both nitrocellulose and nitroglycerin decompose slowly even at the ordinary temperature, and as the temperature is raised the rate of decomposition increases rapidly. Nevertheless, under favorable conditions of storage, a good sample of guncotton can be kept for a great number of years without undergoing serious deterioration. But during manufacture unstable bodies are formed, which are extremely difficult to remove from the nitrocellulose. One class of these bodies is that of the mixed sulphuric and nitric esters of cellulose, which have been mentioned above, but there are also other substances the exact nature of which is unknown at present but which are very deleterious. In the early days of the manufacture of nitrocellulose there were no methods known for readily distinguishing a stable from an unstable explosive, and the result was a series of devastating explosions which practically put a stop for a time to the new industry, and it was only after Sir Frederick Abel had devised his "heat test" that it was possible to carry on the manufacture of modern explosives with safety. Although this test has many imperfections, and a large number of other tests have been proposed to replace it, it is still the one that is most used, as it is very simple and easy to carry out, and the other tests are equally open to objection.

Nearly all the stability tests that have been proposed depend on the detection or measurement of the nitrogen oxides given off when the explosive is heated to a more or less elevated temperature. The first class of these tests is that of the so-called "trace tests," in which the explosive is heated at a moderate temperature, such as 160 or 180°, and the time taken to colour a very sensitive test-paper or solution is observed. The Abel test belongs to this class. The second division is that of the "fume tests," in which the sample is heated at a considerably higher temperature, 100° to 135°, and the time noted until it commences to fume, or until it affects some less sensitive reagent, such as litmus-paper. The third class, that of the "quantitative tests," comprises those in which the guncotton is heated at a fixed temperature within about the same limits as those of the "fume tests," and measurements are made of the amount of the oxides of nitrogen or the total products of decomposition given off in a fixed period of time.

The Abel Heat Test.[1]—The following are the principal appliances required for this test as laid down by the British Home Office. The illustrations of apparatus used in this test are from Appendix VI, Regulations for Army Ordnance Service, Pt. 2; by permission of the Controller of His Majesty's Stationery Office.

> Argand gas burner or Berzelius spirit lamp if gas is not available.
> Needle for piercing heat test-papers.
> Test-tubes 5 1/4 to 5 1/2 in. long, and of such a diameter that they will hold from 20 to 22 c.c. of water when filled to a height of 5 in.
> India-rubber stoppers, No. 4, fitting the test-tubes and carrying an arrangement for holding the test-paper, viz., a narrow glass tube passing through the centre of the stopper, and drawn out so as to form a hook, or terminating in a platinum wire hook. (Fig. 21.)
> A water-oven, measuring inside about 9 in. each way, with wire gauze shelves about 3 in. apart.
> A thermometer.
> A clock or watch.
> Special Water-bath.—This consists of a spherical copper vessel, A (Fig. 22), of about 8 in. diameter with an aperture

[1] For the significance of the Abel Heat Test see Robertson and Smart, *J. Soc. Chem. Ind.*, 1910, 29, 130.

of about 5 in.; it has a loose lid of sheet copper about 6 in. in
diameter, B, and rests on a tripod stand about 14 in. high, C,
which is surrounded by a screen of thin sheet copper, D;
within the latter is placed the Berzelius or Argand burner,

FIG. 21.
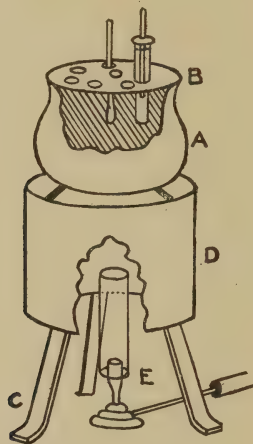
FIG. 22.

E, with copper chimney. The lid, B, has seven holes ar-
ranged as seen in Fig. 23, No. 7 to receive a thermometer and
the other 6 to receive the test-tubes containing the explosives
to be tested. Around each of the holes 1 to 6, on the under-
side of the lid, are soldered 3 pieces of brass wire with points
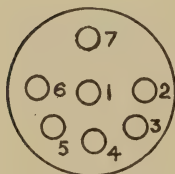
FIG. 23.

FIG. 24.

slightly converging (Fig. 24). These serve to hold the test-
tubes in position and allow them to be easily removed.

A nest of 2 sieves with holes drilled in sheet copper. The
holes in the top sieve have a diameter equal to 14 BWG;

those in the second sieve are equal to 21 BWG. The lower sieve fits into a box also of sheet copper, and the upper sieve is closed with a copper lid. There are standard patterns of sieves and bath, which can be obtained from the usual dealers in chemical apparatus.

Mill.—This also is of standard pattern and can be obtained from the same sources.

Cutter for cutting up Cordite MD and other tough materials.

The test-paper is prepared as follows: 3 grm. of white maize starch (corn-flour) previously washed with cold water are added to 250 c.c. of distilled water, the mixture stirred, heated to boiling and kept gently boiling for ten minutes; 1 grm. of pure potassium iodide (recrystallised from alcohol) is dissolved in 250 c.c. of distilled water. The 2 solutions are thoroughly mixed and allowed to get cold. Strips or sheets of the best white English filter-paper, weighing air-dry 4.1 to 4.6 grm. per 100 square inches (645 sq. cm.), previously washed with water and dried,[1] are dipped into the solution thus prepared, and allowed to remain in it not less than 10 seconds; they are then allowed to drain and dry in a place free from laboratory fumes and dust. The upper and lower margins of the strips or sheets are cut off, and the paper is preserved in well-stoppered or corked bottles *in the dark*. After preparation the papers should be kept (in the dark) for a month before being taken into use. After that, if kept carefully (in the dark), they will remain good for 6 to 12 months, but they should be tested from time to time by putting on one of them a drop of dilute acetic acid, made by mixing 1 volume of acetic acid, b. p. with 4 volumes of distilled water. The freshly prepared paper and that which is still in good condition will give no colouration. In time, however, and soonest in a bright light, a drop of acid produces a brown or bluish colouration. A single hour of strong sunlight causes a marked effect. If the paper is unserviceable, the discolouration takes place at once; any discolouration taking place some time afterward may be disregarded.

The dimensions of the pieces of test-paper used are about 20 mm. by 10 mm. (0.8 by 0.4 in.).

[1] As some English filter-paper has been found to contain some substance soluble in acetic acid, which liberates iodine from potassium iodide, the Home Office authorities now find it advisable to wash the filter-paper twice with dilute acetic acid, made by mixing 1 part of the glacial acid with 10 parts of distilled water, wash all night in running tap water, rinse twice in distilled water, dry, and proceed as above. (Annual Report of H. M. Inspector of Explosives for 1907, p. 17).

Standard Tint-paper.—A solution of caramel in water is made of such strength that when diluted 100 times the tint of the solution equals that produced by Nessler reagent in 100 c.c. of water containing 0.000235 grm. of ammonium chloride. With this solution lines are drawn by means of a clean quill pen on strips of filter-paper previously washed with distilled water to remove traces of bleaching matter and dried. When these marks are dry, the paper is cut into pieces of the same size as the test-paper previously described, so that each piece has a line across it near the middle of its length. Only those strips are used in which the brown line has a breadth of from 0.5 to 1 mm. The standard tint-paper should be kept in a corked tube, and should not be exposed to the light except when actually in use.

Applications of Abel Heat Test.

Guncotton, Compressed Nitrocellulose, Tonite, Etc.—*Preparation of the Sample.*—Sufficient material to serve for 2 or more tests is removed from the centre of the block or cartridge by gentle scraping, and if necessary further reduced by rubbing through a sieve with a clean hard brush. The fine powder thus produced is spread out in a thin layer upon a paper tray 6 in. by 4.5 in., which is then placed on one of the wire gauze shelves of the water-oven, which is kept as nearly as possible at 120° F. (49°). The sample is allowed to remain at rest for 15 minutes in the oven, the door of which is left wide open. After the lapse of 15 minutes the tray is removed, and exposed to the air of the room for 2 hours, the sample being at some point within that time rubbed upon the tray with a brush in order to reduce it to a fine and uniform state of division.

The English War Department method differs from this in specifying that after drying in the oven the guncotton shall be exposed for 4 hours instead of 2.

Application of the Test.—The water-bath is to be filled to within 0.25 in. of the edge. The thermometer is inserted through hole No. 7 of the lid to a depth of 2.5 in. measured from the lid, and the water is heated and maintained at a temperature of 170° F. (76.7°). When this temperature is reached 20 grains (1.3 grm.) of the prepared guncotton are weighed out, placed in the test-tube, and gently pressed down until it occupies a space of not more than 1.3 in. in the test-tube. A test-paper is affixed to the hook of the glass tube and moistened by touching the upper edge with a drop of distilled water containing

50% of pure glycerol. The quantity of liquid used must only be sufficient to moisten about half of the paper. The cork carrying the rod and test-paper is then fixed into the test-tube, and the latter inserted into the bath to a depth of 2.5 in., measured from the cover. The test-paper is to be kept near the top of the test-tube, but free of the cork, until the tube has been immersed for about 5 minutes. A ring of moisture will about this time be deposited upon the sides of the test-tube a little above the cover of the bath; the glass rod must then be lowered until the lower margin of the moistened part of the paper is on a level with the bottom of the ring of moisture in the tube; the paper is now closely watched. The test is complete when the faint brown line, which makes its appearance on the line of boundary between the dry and moist portions of paper, equals in tint the line on the standard tint-paper.

The interval of time between the first insertion of the test-tube in the water at 170° F. and the production of the standard tint constitutes the test, and this interval of time must be *not less* than 10 minutes, or the sample will not be considered to have satisfied the test.

The British War Department directions differ from these in stating that the thermometer and tubes are to be immersed in the water to a depth of 2.5 in., whereas according to the Home Office the 2.5 in. are to be measured from the cover so that only 2.25 in. are immersed in the water.

According to the British Home Office, the glycerol and water are to be applied to the upper edge of the test-paper by means of a camel's-hair pencil, but the chemists of the War Department use a glass rod forming the prolongation of the stopper of a dropping-bottle.

These and other differences appear very trivial, but with such a very delicate test very slight causes produce differences in the results.

Schultze, E C Powder and other Sporting Powders.—These contain a considerable proportion of ungelatinised nitrocellulose, and should be dried, exposed, and tested in the same manner as guncotton.

Cordite, Ballistite.—These and other preparations containing nitrocellulose, gelatinised or semi-gelatinised, are tested as follows:

If the preparation is in the form of small flakes or grains, as is the case with some rifle powders, 1.6 grm. (25 grains) are weighed out into a test-tube. But if the pieces are larger, as in the case of cordite, they must be broken up and ground. Pieces 1/2 in. long are cut from one end of all the sticks of cordite selected for the test, and in the case of

the larger sizes of cordite each piece so cut is further subdivided into 4 portions. These cut pieces are then passed once through the mill, the first portion of material that passes through being rejected on account of the possible presence of foreign matter from the mill. The ground material is put on the top sieve of the nest and sifted. That portion which has passed through the top sieve and been stopped by the second is taken for the test. If the mill is properly set, the greater part of the ground material will be of the proper size.

If too hard for the mill, the material may be softened by exposure to the vapour of acetone or reduced to the necessary state of subdivision by means of a moderately coarse rasp. Should the acetone vapour have rendered it too soft for the mill, it should be cut up into small pieces, which may be brought to any desired degree of hardness by simple exposure to air.

Explosives, which consist partly of gelatinised collodion cotton and partly of ungelatinised guncotton, are best reduced to powder by a rasp or softened by exposure to mixed ether and alcohol vapour at a temperature of 33 to 39° (90 to 100° F.).

If the volatile matter in the explosive exceeds 0.5%, the sifted material should be dried at a temperature not exceeding 140° F. (61°) until the proportion is not more than 0.5%.

After each sample has been ground, the mill must be taken to pieces and carefully cleaned.

The British War Department regulations, on the other hand, do not allow of softening the cordite with acetone vapour. For *new* cordite supplied to the department by contractors it is specified that 1/4 in. shall be cut from every stick forming the sample and discarded. Small pieces or slices about 1/8 in. thick are then cut off and passed through the mill, the first portion being rejected. The portion that passes through the first sieve, but is stopped by the second, is used for the heat and moisture tests, whereas the finer portion which passes through the second sieve is used for the rest of the analysis. The material used for the heat and moisture tests should not pass through the mill more than once, else there will be some loss of moisture. For the same reason it should be put at once into well-stoppered bottles and should not be touched with the hands.

In the case of *old* cordite, which has already been issued to the services, it is permitted to pass the material which remains on the top sieve through the mill once again, but not oftener. No delay should

take place between the grinding of the cordite and the carrying out of the test, and aeration should be avoided. The adjustment of the percentage of volatile matter to 0.5 is, therefore, directly contrary to the Service regulations, although recommended by the British Home Office.

For the application of the test the Home Office instructions are as follows: The thermometer is fixed so as to be inserted through the lid of the water-bath (Fig. 22, p. 596) into the water to a depth of 2.75 in. The water is to be maintained at a constant temperature of 180° F. (82.2°). A test-paper is fixed on the hook of the glass rod, so that when inserted into the tube it will be in a vertical position. It is moistened with glycerin and water as directed above for guncotton. The cork carrying the rod and paper is fixed into the test-tube and the position of the paper adjusted so that its lower edge is about half-way down the tube, which is then inserted through one of the holes in the cover of the bath to such a depth that the lower margin of the moistened part of the paper is about 0.6 in. above the surface of the cover. The test is completed when the faint brown tint, which after a time makes its appearance at the margin between the wet and dry portions of the test-paper, equals in depth of tint the brown line drawn on the standard tint-paper. The time which elapses between the insertion of the test-tube into the bath at 180° F. and the completion of the test must not be less than 15 minutes, according to the Home Office regulations.

No new cordite is accepted by the War Department from contractors unless it stands a heat test of 30 minutes at 180° F., but the test is carried out with papers that are less sensitive than those of the Home Office.

Cordite, which has already been issued to the Services, is tested at 160° F. (71.1°). If the test is 8 minutes or above, the cordite is considered "serviceable"; if below 8 minutes and above 4 minutes, it is "doubtful" or "unserviceable."

Nitroglycerin.—As nitroglycerin by itself is not an article of commerce, the British Home Office does not find it necessary to specify a test for it, but only for nitroglycerin extracted from such materials as dynamite and for nitroglycerin explosives. The War Department, however, specifies a test for the nitroglycerin that is used in the manufacture of cordite. For this 6.5 grm. (100 grains) are taken and passed through a neutral filter-paper to remove moisture. Of the filtrate 3.25 grm. (50 grains) are introduced into a test-tube, and the

test is carried out as in the case of cordite. It must give a test of at least 18 minutes at 180° F.

Dynamite.—Nitroglycerin explosives, from which the nitroglycerin can be removed mechanically, must satisfy the following test laid down by the Home Office: This test, however, though looked upon at present as the most important, so far as testing the purity of the nitroglycerin is concerned, is only one of several which any given sample of nitroglycerin preparation has to satisfy in order to establish its compliance with the definition in the Authorised List.

About 20 or 26 grm. (300 or 400 grains) of dynamite, finely divided, are placed in a funnel 2 in. in diameter, which has previously been plugged with some freshly ignited asbestos. The surface is smoothed by means of a flat-headed glass rod or stopper and some clean washed and dried kieselguhr is spread over it to a depth of 1/8 in. Water is next carefully dropped from a wash-bottle upon this kieselguhr, and when the first portion has been soaked up, more is added; this is repeated until sufficient nitroglycerin has been collected in the graduated measure below. If any water should have passed through with the nitroglycerin, it should be removed with a piece of blotting-paper, and the nitroglycerin, if necessary, filtered through a dry filter-paper.

Application of the Test.—3.25 grm. (50 grains) of the nitroglycerin are weighed into a test-tube in such a way as not to soil the sides of the tube, and the test is carried out as in the case of cordite, except that the temperature of the bath is 160° F. (71.1°). The nitroglycerin will not be considered to have satisfied the test unless the time necessary to produce the standard tin is at least 15 minutes.

Blasting Gelatin, Gelatin Dynamite, Etc.—3.25 grm. (50 grains) of blasting gelatin are intimately incorporated with 6.5 grm. (100 grains) of French chalk. This can be effected by working the materials with a wooden pestle in a wooden mortar. The French chalk should be of good commercial quality, should be carefully washed with distilled water, dried in a water-oven, and exposed under a bell jar to moist air until it has taken up about 0.5% of moisture. It should be bottled for use, and with ordinary care the percentage of moisture will not alter much.

The mixture is to be gradually introduced into a test-tube of the dimensions prescribed above with the aid of gentle tapping on the table between the introduction of successive portions of the mixture

into the tube, so that when the tube contains all of the mixture it shall be filled to the extent of 1.75 in. of its height. The test-paper is then to be inserted and the heat applied in the manner prescribed above. The sample tested is to withstand exposure to 160° F. (71.1°) for a period of 10 minutes before producing a discolouration of the test-paper corresponding in tint to the standard tint-paper.

Non-gelatinised nitroglycerin preparations, from which the nitroglycerin cannot be expelled by water, are tested without any previous separation of the ingredients, the temperature being, as above, 160° F. and the time 7 minutes.

United States Directions for the Heat Test.—The regulations issued by the military and naval authorities of the United States differ considerably from the English ones: in some respects they are more explicit, in others less so. They are here given in full:

Blasting gelatin, gelatin dynamite, and analogous preparations are also submitted to liquefaction and exudation tests, which are identical with those prescribed by the United States Government, *q.v.* below, p. 605.

Nitroglycerin.—The water-bath of the potassium-iodide-starch testing-apparatus is brought to 160° F. (71.1°), and maintained at that temperature, being regulated by the thermometer which should be immersed about 2 3/4 in. in the water. The source of heat should be carefully watched, and at no time should the temperature of the bath rise or fall more than 1° F. from 160° F. 50 grains of nitroglycerin are placed in each test-tube and carefully weighed, being careful not to get any on the sides of the test-tube; this may be done by using a suitable dropper or glass tube.

A piece of test-paper is taken with the pincers and laid down on a piece of clean filter-paper. The test-paper is held in place by the end of a glass rod which has been thoroughly cleaned, heated, and cooled. A small hole is made in the test-paper with the point of the pincers opposite the middle of one end of the paper and about 0.2 in. from the edge. The test-paper is taken up with the pincers, the platinum hook inserted through the hole just made, the hook bent with the pincers until the throat of the hook is closed tightly on the paper so that it will stand stiffly up when the paper is held vertically above the glass rod. The glass rod with test-paper is placed carefully aside under a bell glass or other protecting cover where it will be protected from fumes and dust. In the same way the other test-papers are prepared.

A solution of pure glycerol and distilled water, in equal volumes, is prepared.

One of the test-papers is taken, held with the paper up, and a drop of the glycerol solution is placed on each of the lower corners of the test-paper, as held; the paper should absorb this evenly about half-way to the opposite upper edge, leaving a distinct line about midway between the moistened and the unmoistened parts. One of the test-tubes is placed in the bath through one of the apertures in the cover and is immersed until the sample is below the surface of the water. The test-paper, moistened with glycerol, is placed in the test-tube, and the glass rod is moved through the cork until the line between the moistened and unmoistened parts of the test-paper is about 5/8 of an in. above the upper surface of the cover. This time is recorded. The same is done with each of the other 2 test-papers. The line between the moistened and unmoistened parts of each test-paper is watched carefully, and the exact instant that a faint brown colour[1] appears on this line of demarcation on each test-paper is recorded. This completes the test.

The nitroglycerin under examination will not be considered "thoroughly purified" unless the time elapsed between the insertion of the test-paper and the appearance of the brown colour is at least 15 minutes. The average of the records of all the tubes will be taken.

Explosive Gelatin.—If explosive gelatin is under examination a sample of 50 grains is intimately incorporated with 100 grains of French chalk, using a wooden pestle in a wooden mortar. The French chalk should be of good commercial quality, should be thoroughly washed with distilled water, dried in a water-oven, and then exposed to moist air under a bell jar until it has taken up about 0.5% of moisture. It should then be placed in a glass-stoppered jar for use.

Each test-tube is filled with this mixture to a depth of 1 3/4 in., the tube being gently tapped on a table to insure a proper degree of settling.

The heat test is then conducted as explained for nitroglycerin. Explosive gelatin will not be considered as serviceable unless the average time of the test is at least 10 minutes.

Explosive gelatin is subjected also to a liquefaction and exudation test as follows:

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[1] In order to detect this colour promptly, the water-bath should be so placed that a bright reflected light falls on the papers.

Liquefaction Test of Explosive Gelatin.—A cylinder is cut from the cartridge having its height equal to its diameter, care being taken to have the ends cut flat and true.

This cylinder is placed on a piece of filter-paper on a smooth clean board, and secured to the board by an ordinary pin forced through it along its axis into the board.

It is exposed in this condition for 144 consecutive hours to a temperature ranging from 85 to 90° F.

The original height of the cylinder should not decrease more than 1/4 and the upper cut surface should retain its flatness and sharpness of edge.

Exudation Test of Explosive Gelatin.—There should be no separation of nitroglycerin in the liquefaction test or under any conditions of storage, transport, or use, or when the explosive is subjected three times in succession to alternate freezing and thawing.

Loose-fibre Guncotton.—The material is dried at a temperature not greater than 40° to constant weight; then exposed on trays to the air in a room free from fumes, until from 1 to 2% of moisture has been absorbed. It is then gently rubbed through a ten-mesh sieve to insure uniformity of division, being careful that it does not come in contact with the hands or any piece of apparatus not perfectly free from any trace of acid or alkali. 1.3 grm. are weighed out and placed in a test-tube 5 1/2 to 6 in. long and not less than 1/2 in. internal diameter.

The potassium-iodide-starch test is conducted as explained for nitroglycerin, except that the water-bath is heated to 150° F. (65.5°). The test-papers, prepared as already explained, are inserted in the test-tubes[1] and the papers adjusted in the tubes so that the line dividing the dry and moist portions of the test-paper is on a level with the lower edge of the film of moisture which is deposited on the side of the tube soon after inserting it in the bath.

Nitrocellulose intended for the manufacture of smokeless powder must not show a brown colour in less than 40 minutes (Army), (Navy, 30 minutes) at 150° F. (65.5°).

Blocks or Discs.—Guncotton for demolition purposes is issued in the form of compressed pulp in discs or blocks. This form of guncotton is prepared for the heat test as follows:

Sufficient material to serve for 2 or more tests is removed from the

[1] The standard water bath for nitrocellulose holds ten tubes; it is long and narrow to prevent heating the upper part of the tubes as much as possible. Tubes are immersed 2 3/4 in. in the bath.

centre of a block or disc by scraping, and reduced to a fine powder
by rubbing between pieces of clean, dry filter-paper.   This is spread out
in a thin layer upon a paper tray about 6 by 4 1/2 in., which is then
placed inside a water-oven, kept as nearly as possible at 120° F. for
15 minutes, the door of the oven being left wide open.   The tray is
then removed and exposed to the air of the room for 2 hours; during this
time the material is rubbed on the paper tray with a clean glass rod
and reduced to a fine and uniform state of division.

The temperature of the water-bath is the same as for fibre guncotton
(150° F.).

There should be no brown within 10 minutes.

Poacher Sample.—In case the sample is taken during the manu-
facture of nitrocellulose, it is taken after the poaching and after having
been thoroughly washed in pure cold water.   The sample is pressed
dry in a hand press and rubbed in a clean cloth until finely divided,
being careful not to let it come in contact with the hands.

Smokeless Powder.—The sample should be prepared by cutting
into slices 0.02 in. thick.   These slices are exposed to the air for at
least 12 hours.

The test-tube sample consists of 1.3 grm.

The usual potassium iodide test is followed, except that the tempera-
ture is considerably higher for simple nitrocellulose powders, being
100° (212° F.) instead of 65.5° (150° F.).   Each sample must stand
this temperature without showing a brown line for 10 minutes.

Powders containing nitroglycerin should stand the test at 65.5° for
20 minutes.

Precautions.—It is of the utmost importance that all the opera-
tions connected with the Abel and other trace tests be conducted in a
room that is quite free from acid fumes, as the test is affected by very
minute traces of acids and other bodies.   It has been calculated by
Will that the quantity of nitrous acid necessary to affect heat-test paper
corresponds to 4×10^{-5} mg. of nitrogen.   If heat tests have to be carried
out frequently, it is best to keep a special room for the purpose or,
better still, a special building remote from any place where acid or other
fumes are generated.   The operator also must be careful not to intro-
duce anything that can affect the test: he should wash his hands before
starting the test and should not wear clothes that can have become
contaminated.

In 1901, Cullen called attention to the desirability of having a uniform

official source for the heat-test papers used throughout the British Empire (*J. Soc. Chem. Ind.*, 1901, **20**, 8), as very trifling differences in the method of preparation affect the results considerably. All contractors for explosives to the Government can now obtain heat-test papers made at the Royal Gunpowder Factory, Waltham Abbey, identical with those used by the War Department inspectors throughout the Empire. The Home Office also supplies heat-test papers to their inspectors and to manufacturers of explosives. Unfortunately, the War Department papers are not the same as those of the Home Office, as they are made from a thicker filter-paper, and are consequently less sensitive. The War Department recommends that the papers be kept for 6 weeks before use, instead of 1 month, as laid down by the Home Office.

The United States Government also issues heat-test papers to the manufacturers who contract to supply it with explosives.

If heat-test papers from other than the official source be used, it is necessary to compare them with the official papers as regards sensitiveness. This may be done by having glass rods with two platinum hooks side by side, and hanging on each of them one of the papers to be compared. The heat test is then carried out in the usual way and if there is a small difference in the time in which the standard tint appears, a correction is applied to all the results obtained with the papers in question. If the difference is large, the papers should be discarded.

The objections to the test are due to its extreme sensitiveness. On the one hand, samples that are really stable sometimes give low heat tests, because they have become contaminated with minute traces of some material which is really harmless but affects the iodide and starch paper; ozone, for instance, has a powerful effect. On the other hand, samples of insufficient stability sometimes give high tests, because they contain traces of some substance that interferes with the reaction between the oxides of nitrogen and the paper. *Mercuric chloride* is a substance of this kind, for an extremely small proportion will lengthen the heat test of the sample very considerably. In Germany it has been usual to carry out the final washing of guncotton with water containing a little of this salt, ostensibly in order to prevent the growth of fungus on the guncotton; but this object can be better achieved by using phenol, and it seems probable that the real object is to improve the heat-test. At any rate, this is the view that has always been taken by the authorities

in England, and they regard the addition of mercuric chloride or any similar masking agent as a most reprehensible practice.

Until recently there was no test known which would detect these minute proportions of mercury in an explosive, but the late Dr. A. Dupré, chemical adviser to the Home Office, worked one out which enabled him, in 1906, to detect it with certainty in some blasting gelatine made by Messrs. Kynoch, Ltd., which had behaved in a suspicious manner. He then applied the test to the cordite made by the same firm, and found mercury again. In consequence of this legal proceedings were taken. The methods used for the detection of mercury in explosives are given by Messrs. F. H. and P. V. Dupré in the Annual Report of H. M. Inspectors of Explosives for 1907, p. 17, and are as follows:

British Home Office Tests for Mercury.

The apparatus employed for this test consists of two stoppered tubes of about 20 c.c. capacity, joined by a capillary tube. To one stopper is attached a tube fitted with a good tap. All the grinding must be done very perfectly so as to keep a vacuum for some hours even at a slightly raised temperature. About the centre of each tube the electrodes, contained in tubulars slanted up so as to prevent the entrance of explosive material, are attached. The parts of the tubes below these tubulars are filled with the substance to be examined, the stoppers are replaced, and the tube exhausted by means of a good pump (not a mercury pump). The parts of the tube containing the explosive are then immersed in hot water (about 90°), and a discharge from a powerful induction coil (6 in. spark) passed through it. The capillary tube is then examined end on: if a condenser is used, the spectrum is greatly intensified. If mercury or a volatile mercury salt be present even in very minute quantities, the characteristic lines of the mercury spectrum are seen in addition to those of any other gases that may be present, such as nitrogen, oxygen, and hydrogen. The spectrum of nitrogen may be eliminated by passing a stream of hydrogen through the cold tube before exhausting; after exhaustion, practically only the spectra of mercury, if present, hydrogen and oxygen will then be seen. The hydrogen and oxygen spectra can never be eliminated, as it is impossible to get rid of the last traces of moisture; but this does not in any way interfere with the spectrum of mercury.

The lines relied on for proving the presence of mercury are the two yellow, the green, and the violet of the following wave lengths: the yellow 5790 and 5769, the green 5461, and the violet 4359. The presence of mercury is not certified, unless all these lines are seen. All the apparatus used, tube, connections, etc., must be carefully tested to prove the absence of mercury before each test is carried out.

Ungelatinised Guncotton.—About 2 grm. of the nitrocotton are carefully dried at a temperature not exceeding 120° F. (49°), introduced into the special vacuum tube, and the test carried out as described above.

Blasting Gelatin, Gelignite, etc.—About 4 grm. of the explosive are ground up with French chalk, introduced into the vacuum tube and tested as above. If the explosive contains a considerable amount of moisture, the introduction of a piece of calcium chloride above the explosive in each limb may be of considerable value. Blank experiments must be made with the chalk used before the test is carried out.

Cordite.—15 grm. of the cordite are ground so as to pass through the finest sieve of the heat-test set, and extracted with ether for 2 hours. The flask is then removed, and a carefully cleaned flask substituted; fresh ether is introduced and the extraction continued for a further 10 hours. The ether is then distilled off, and the flask carefully dried at a low temperature. The flask is washed out with several quantities of distilled water, a little hydrochloric acid being added to the first boiling. The washings are put into a previously ignited platinum dish, and the solution electrolysed overnight, using the dish as anode and a coil of platinum or gold wire as kathode. Two Leclanché cells are used in series for the electrolysis. The wire is then washed with water and acetone, dried at a low temperature, dropped into a clean narrow test-tube (3 in. by 3/8 in.), and the part of the tube containing the wire strongly ignited. The bottom of the tube is cut off after removing the wire, and the remainder dropped into the vacuum tube and tested for mercury, as already described.

Hard Gelatinised Nitrocotton Preparations.—These are treated exactly as cordite, unless the explosive contains nothing, which is soluble in ether, other than a mercury salt, in which case the preliminary 2 hours' extraction with ether is omitted.

Specially Delicate Tests.—If an ungelatinised nitrocotton has to be tested for very minute traces of soluble mercury salts, any desired

quantity can be extracted with ether, and treated as described above for hard gelatinised nitrocotton explosives.

Metallic Mercury.—All the above tests, in which extraction by ether is employed, are of course only tests for soluble mercury salts, not for metallic mercury. The following very delicate test may be used for blasting gelatin or any other explosive when only metallic mercury is sought.

15 grm. or any other quantity, according to the degree of delicacy required, are ground up with French chalk and introduced into a stoppered bottle. A piece of silver foil is ignited in a combustion tube, through which a slow current of hydrogen is passed. This foil is then placed in a glass spoon on top of the explosive, and the bottle is tightly stoppered and kept at a temperature of 90 to 100° for 10 to 15 hours. The silver foil is then treated in the same way as the coil in the cordite test.

Considerable difficulty has been experienced by firms who have been using mercury in their expolsives in the past in getting their plant free from all traces of the salt. Even 6 months after the last addition of mercury the explosive still contains enough to very seriously affect the heat test. In this connection it may be of service to point out what an extremely minute amount of mercury may affect the result. From quantitative experiments it was found that even 0.001 mg. of mercury can combine with as much iodine as would be liberated by an average sample of blasting gelatin in the 5 minutes after the standard tint on the test-paper was reached, or, in other words, is capable of masking the heat test to the extent of 5 minutes.

With reference to the rejection of explosives on account of their containing mercury, it has been suggested that the main objection to its use, viz., its effect on the heat test, might be overcome by introducing a piece of silver foil into the tube during the test. It was alleged that the mercury was thus entirely retained by the silver and that the true test of the explosive was obtained. This point was therefore investigated, but it was found that, although the effect of the mercury on the test-paper was undoubtedly counteracted and a test that had been much prolonged by the presence of mercury was considerably shortened, yet the silver itself had a considerable masking effect, probably due to absorption of the acid vapours by the silver. It was therefore considered that, although the above test might be useful as a supplementary test for the presence of mercury, it could not be considered

to remove the objections to the use of mercury in explosives. The use of gold foil was also suggested, but although preferable to silver for use with nitrocottons, in that its masking effect is considerably less, yet, as it decomposes nitroglycerin vapour, it cannot be used with nitroglycerin explosives.

Microscopic Test for Mercury.—Hargreaves and Rowe, of the Government Laboratory, South Australia, have worked out a process in which the microscope is used instead of the spectroscope (*J. Soc. Chem. Ind.*, 1907, **26,** 813). 100 grm. of blasting gelatin, gelatin dynamite, gelignite, etc., are ground up in a mortar with 100 grm. of purified French chalk, the grinding being done in small quantities at a time. The mixture is placed in a flask in a water-oven and connected by glass tubing passing out of the water-oven to a Woulff's bottle or other absorption apparatus containing 50 c.c. of water and 75 c.c. of strong sulphuric acid, and the whole gently aspirated, while the flask is heated in the bath to the temperature of boiling water. In about 2 hours the mercuric chloride will be transferred to the dilute sulphuric acid in the absorption apparatus. The solution is then subjected to electrolysis, a pure gold kathode and platinum anode being used. The current required is about 0.5 ampère or less at a pressure of 2 volts. The deposition of the mercury on the gold is complete in a few hours, but the current may conveniently be left going all night. When the quantity of mercury is large, the gold kathode will be seen to be coated with mercury, and it may be weighed, and the test thus made quantitative, but, as a rule, there will not be sufficient deposit to be visible. The gold foil is removed from the electrolyte, while the current is still running, washed in distilled water, then alcohol, dried, rolled into a cornet, and inserted into a glass tube 6 mm. in diameter, sealed at one end and expanded at the other and ground flat to fit closely against a glass microscope slide. The glass tube is fitted in a hole in a stout brass plate and then very gently heated after a dry microscope slide has been placed on top. A sublimate will be obtained on the glass slide, and care must be taken not to raise the temperature sufficiently to revolatilise this. The slide on being examined under the microscope at a magnification of about 250 diameters by transmitted and reflected light will show globules of metallic mercury of large or small size according to the skill with which the heating has been conducted. If the globules are very small, they may not be readily recognised as mercury, but under the conditions of the method any small opaque

dots showing brilliant specks by reflected light must be mercury, and a repetition of the test will probably show larger globules.

Other Trace Tests.

Zinc Iodide and Starch Test.—In Germany, the Netherlands, and some other countries a modification of the Abel test is used, zinc iodide being substituted for potassium iodide, and it is claimed that the test is thereby rendered more sensitive. This, however, is hardly an advantage, as the principal fault of the Abel test is its excessive sensitiveness. In Spain a paper is used impregnated with a solution containing starch, zinc iodide, and zinc chloride.

Guttmann's Test.—Guttmann carried out a series of experiments to find a reagent which would not be masked by solvents such as ether-alcohol and ethyl acetate nor by such substances as mercuric chloride (*J. Soc. Chem. Ind.*, 1897, 16, 293). He decided upon a paper impregnated with diphenylamine in sulphuric acid solution. Of the diphenylamine 0.100 grm. is dissolved in 40 c.c. of water together with 10 c.c. of concentrated sulphuric acid, and when cold an equal volume of pure glycerol is added. Filter-paper is well washed, dried, and cut into strips 1.0 in. by 0.4 in. One of these strips is suspended from a hook, as in the Abel heat test, and the top edge is moistened with 2 drops of the reagent, so that they run together and cover about a quarter of the paper. Otherwise the test is carried out like the Abel test at a temperature of 70°. The moistened part of the paper after a time becomes greenish-yellow and then a dark blue mark appears at the dividing line between the moist and dry parts of the paper. This is the end of the test. The test has been adopted by the Belgian military engineers and is in use in several other countries, but unfavorable reports have been made by several investigators who have been unable to obtain concordant results with this test.

Spica's Test.—In this test m-phenylene diamine hydrochloride and cane-sugar are used to impregnate the paper. The reagent is much more sensitive than potassium iodide and starch, and for this reason has not been adopted extensively.

Several other "trace tests" have been proposed, but none of them have come into general use.

Fume Tests.

Vieille Test.—In this test the explosive is heated at 110° in a closed tube with litmus-paper in a specially designed bath. The quantity

of explosive taken is 10 grm., preferably in one piece; this is heated in the bath for a day of 8 hours or until the litmus-paper has assumed a standard red tint. Next day this is done again with a fresh piece of litmus-paper, and the procedure is repeated until the litmus-paper is reddened in 1 hour. All the times are then added together and the total time is noted. This test has been adopted officially in France and is also used considerably in other countries, but it is considered by some investigators to be unreliable (see Sy, *J. Franklin Institute*, 1908, **166,** pages 249, 321 and 433).

German 135° Test.—This is a test which is much used for nitro-celluloses. The following are the particulars of the method as carried out in the United States Ordnance Laboratory (see Sy, *J. Franklin Inst.*, as above, also *J. Amer. Chem. Soc.*, 1903, **25,** 550).

2.5 grm. of the sample to be tested are dried at the ordinary temperature of the laboratory for 12 hours and placed in a strong test-tube. A piece of blue litmus is placed in the tube about 1/2 in. above the sample, the paper being folded lightly so as to give the folds sufficient elastic power to hold the paper in place by pressure against the sides of the tube. The tube is lightly closed by a cork with a hole 0.15 in. diameter bored through it, and so placed in a bath of boiling xylol (the b. p. of which is 135°) that only 6 or 7 mm. project above the surface.

Examination of each tube is made each 5 minutes after 20 minutes have elapsed. In making this examination the tube should be withdrawn only 1/2 its length and quickly replaced.

2 tubes are used in each test, and there must be no failure in either tube.

Three observations are made: 1. Time of *complete* reddening of litmus-paper; 2. time of appearance of brown nitric oxide fumes; 3. time at which the sample exploded.

Stable explosives should give the following times:

	Litmus not reddened in	No nitric fumes in	No explosion in
Uncolloided nitrocellulose......	30 min.	45 min.	5 hrs.
Pure nitrocellulose powder....	1 hr. 15 min.	2 hrs.	5 hrs.
Nitroglycerin powders	30 min.	45 min.	5 hrs.

For the results to have value they should be compared with that of a known stable explosive of the same kind, under the same test by the same operator, using the same test-paper.

Ungelatinised nitrocellulose should be well shaken down in the tube by tapping, or lightly pressed down.

Explosion Test. (See Sy, *J. Frank. Inst.*, as above).—A small sample of the explosive, usually 0.1 grm., is placed in a small test-tube, which is then tightly corked and placed in a paraffin bath at 100°. The bath is now stirred and heated so that the temperature increases 5° per minute. The temperature is noted at which the sample explodes. The following are the lower limits of the explosion temperatures for satisfactory samples, as required by the United States Ordnance Department:

Nitrocellulose.. 186°
Nitrocellulose powder............................... 177°
Nitroglycerin .... 170°

The results are found to be reliable when the explosive is either very good or very bad. Variations in the results may be caused by differences in manipulation, especially in the rate of raising the temperature.

Waltham Abbey Silvered Vessel Test.—This is a test which has been adopted by the British War Department for the examination of cordite which has been in the Service for some time and gives a low heat test. It has been designed to imitate the conditions of storage as closely as possible; at present it is only applied if the heat test at 160° F. is below 8 minutes and above 4 minutes. Full instructions for carrying out the test are given in the "Regulations for Army Ordnance Services, Part II" (Wyman & Sons, 1908), pp. 162 to 167. The cordite is ground as for the heat test and about 50 grms. are placed in a glass vessel surrounded with a vacuum jacket silvered to reduce loss of heat. To the neck of the vessel and at right angles to it is fused a long tube, in order to be able to observe any red fumes as soon as they are given off. A thermometer is introduced through the neck into the centre of the powder. These vessels are placed in recesses in the top of a bath, which is maintained at such a temperature that the thermometers indicate 80° ± 0.1°. After a time red fumes will appear in the side tube, and a few hours later the temperature of the cordite begins to rise. The time is noted when the temperature has risen 2.0°. A good cordite when new will stand this test for 500 or 600 hours. When the test has fallen below 200 hours the cordite is considered "unserviceable" and is destroyed. The test should be carried out in a special building in consequence of the danger of explosion of the considerable quantities of cordite involved. The

temperature of the bath is kept constant by using a Lowry regulator (see Introduction, Vol. 1), if a gas supply be available; if not, the bath must be provided with a reflux condenser and filled with a liquid which boils at the right temperature; a mixture of water and methylated spirit is suitable.

Quantitative Tests. Will Test.—In this 2.5 grm. of dried nitrocellulose are heated in a bath at 135° in a current of carbon dioxide. The gases are passed over heated copper and copper oxide asbestos, and then through strong potash solution, and the residual gas, which is nitrogen, is measured every 15 minutes. A good guncotton gives a steady evolution of about 1.25 mg. of nitrogen per hour from 2.5 grm.; a bad one gives a higher and more irregular evolution. For particulars of the method see Will, *Mittheilungen der Centralstelle*, Neu Babelsberg, 1900, 2, also Robertson, *J. Soc. Chem. Ind.*, 1901, **20**, 609. The apparatus is somewhat expensive and very great care and constant attention are required to obtain satisfactory results.

Bergmann and Junk Test.—The Prussian military authorities have adopted a test devised by Bergmann and Junk (*Zeits. ang. Chem.*, 1904, 982). It has the merit of being quantitative and does not require such an

FIG. 25.

elaborate apparatus as the Will test. In this test the guncotton is heated in a glass tube at 132°, and the nitrous gases are absorbed in water, and when the heating is finished they are estimated by the Schultze-Tiemann method. The heating is carried out in a thick-walled glass tube 35 cm. long and 2 cm. internal diameter. Into the neck is ground a hollow glass stopper, which is surmounted by the absorption apparatus shown in Fig. 25.

The heating bath is a rectangular copper vessel 35 cm. x 10 cm. x 25 cm. high, with 10 tubes, each 20 cm. long, let into it to take the glass tubes. It is also fitted with a reflux condenser and a small tube to take a thermometer; it is filled with amyl alcohol, which is kept boiling.

In the original paper there is a description of an elaborate wooden cupboard to hold the testing apparatus, so that in case of an explosion the effects may be confined. It is, however, expensive and greatly increases the danger of fire. A large piece of plate glass should be erected in front of the apparatus with a piece of woven wire of coarse mesh before it, and there should be an arrangement of cords and

pulleys to enable the operator to remove any tube from the bath without handling it.

The guncotton is dried in a bath with a good current of air at a temperature of 50° C. Then it is passed through a sieve and the drying is continued in a desiccator over sulphuric acid until it contains not more than 1% of water. 2 grm. are weighed out and introduced into the tube of the apparatus, any particles adhering to the sides being removed by knocking the tube or brushing it down with a feather. The glass stopper is slightly lubricated with good mineral lubricating oil and is inserted, the beaker is half-filled with water, and the glass tube is introduced into one of the holes in the bath, which should be at a temperature of 132°. The heating is continued for 2 hours or other convenient time, and then the tube is removed from the bath. As the air in the tube contracts the water is drawn out of the beaker, onto the cotton. The absorption apparatus is washed out into the tube, and the volume is made up to the 50 c.c. mark which is on the tube. The liquid its then filtered, 25 c.c. of the filtrate are taken, 1 c.c. of N/2 potassium permanganate solution is added to oxidise the nitrous to nitric acid, and the nitrogen is estimated by the Schultze-Tiemann method (q. v. above). A good guncotton in 2 hours should not give more than 2.5 c.c. of nitric oxide. The results obtained agree well with those of the Will test.

The U. S. Army Ordnance 115° Test (for Nitrocellulose Powders).—Whole pieces of powder are carefully weighed on watchglasses and then heated in a bath kept at 115°+or−1/2° for 8 hours. The sample is then removed, allowed to cool in a desiccator, and reweighed. This is repeated six times on six separate days. At the end of this time the total loss of weight should not exceed 8%, if the powder is stable enough for military purposes.

The bath may be maintained at 115° by filling the walls of the oven with a properly proportioned mixture of xylol and toluol. A reflux condenser prevents loss of the liquid by evaporation.

The temperature, 115°, is the one that most clearly differentiates the decomposition of good powders from bad ones in a reasonable time limit. If a lower temperature is used, it requires too long a time to establish trustworthy data; if a higher temperature is used, the curves plotted to show the rate of loss of weight of good powders are not so clearly separated from those plotted to show the same for bad powders. (See Sy, *J. Amer. Chem. Soc.*, 1905, **25**, 550.)

[**Photographic Flash Powders.**—Although not usually classed as explosives many of these preparations are dangerous, ignorance of this fact having led to loss of life and property. As a rule, magnesium powder is used with some oxidising agent. In the older formulæ potassium permanganate, potassium dichromate and potassium chlorate were used. Picric acid was frequently added. Such mixtures are dangerous even when freshly prepared, and become still more so on keeping as picrates are formed. A mixture of magnesium (or aluminum) powder, barium nitrate, sodium chloride and amorphous phosphorus was introduced and regarded as safe but an explosion in Philadelphia did much damage. One of the most used powders used in the United States consists of magnesium powder, chlorate of potash and a little red phosphorus.

Analysis of such preparations can generally be made by inspection. The ingredients are not usually ground fine, and can be picked out under a lens of moderate power. Water will dissolve the oxidizing agents. Such substances as magnesium and amorphous phosphorus are left in the residue.—H. L.]

TABLE FOR

COMPARISON OF CENTIGRADE AND FAHRENHEIT DEGREES.

All degrees are + unless otherwise marked.

$1° F. = 0.55° C.$
$1° C. = 1.8° F.$

C.	F.	C.	F.	C.	F.
2000.0	3632.0	1371.1	2500.0	800.0	1472.0
1900.0	3452.0	1300.0	2372.0	760.0	1400.0
1800.0	3272.0	1200.0	2192.0	704.4	1300.0
1700.0	3092.0	1100.0	2012.0	700.0	1292.0
1648.7	3000.0	1093.3	2000.0	648.8	1200.0
1600.0	2912.0	1000.0	1832.0	600.0	1112.0
1500.0	2732.0	900.0	1652.0	593.3	1100.0
1400.0	2552.0	815.5	1500.0	537.7	1000.0

C.	F.	C.	F.	C.	F.
537.7	1000.0	421.1	790.0	304.4	580.0
532.1	990.0	420.0	788.0	300.0	572.0
530.0	986.0	415.6	780.0	298.6	570.0
526.6	980.0	410.0	770.0	293.1	560.0
521.1	970.0	404.4	760.0	290.0	554.0
520.0	968.0	400.0	752.0	287.6	550.0
515.6	960.0	398.6	750.0	282.1	540.0
510.0	950.0	393.1	740.0	280.0	536.0
504.4	940.0	390.0	734.0	276.6	530.0
500.0	932.0	387.6	730.0	271.1	520.0
498.0	930.0	382.1	720.0	270.0	518.0
493.2	920.0	380.0	716.0	265.6	510.0
490.0	914.0	376.6	710.0	260.0	500.0
487.7	910.0	371.1	700.0	259.4	499.0
482.1	900.0	370.0	698.0	259.0	498.2
480.0	896.0	365.6	690.0	258.9	498.0
476.6	890.0	360.0	680.0	258.3	497.0
471.1	880.0	354.4	670.0	258.0	496.4
470.0	878.0	350.0	662.0	257.8	496.0
465.6	870.0	348.6	660.0	257.2	495.0
460.0	860.0	343.1	650.0	257.0	494.6
454.4	850.0	340.0	644.0	256.6	494.0
450.0	842.0	337.6	640.0	256.1	493.6
448.6	840.0	332.1	630.0	256.0	492.8
443.1	830.0	330.0	626.0	255.5	492.0
440.0	824.0	326.6	620.0	255.0	491.0
437.6	820.0	321.1	610.0	254.4	490.0
432.1	810.0	320.0	609.0	254.0	489.2
430.0	806.0	315.6	600.0	253.9	489.0
426.6	800.0	310.0	590.0	253.3	488.0

C.	F.	C.	F.	C.	F.
253.0	487.4	236.6	458.0	220.0	428.0
252.8	487.0	236.1	457.0	219.4	427.0
252.2	486.0	236.0	456.8	219.0	426.2
252.0	485.6	235.5	456.0	218.9	426.0
251.6	485.0	235.0	455.0	218.3	425.0
251.1	484.0	234.4	454.0	218.0	424.4
251.0	483.8	234.0	453.2	217.8	424.0
250.5	483.0	233.9	453.0	217.2	423.0
250.0	482.0	233.3	452.0	217.0	422.6
249.4	481.0	233.0	451.4	216.6	422.0
249.0	480.2	232.8	451.0	216.1	421.0
248.9	480.0	232.2	450.0	216.0	420.8
248.3	479.0	232.0	449.6	215.5	420.0
248.0	478.4	231.6	449.0	215.0	419.0
247.8	478.0	231.1	448.0	214.4	418.0
247.2	477.0	231.0	447.8	214.0	417.2
247.0	476.6	230.5	447.0	213.9	417.0
246.6	476.0	230.0	446.0	213.3	416.0
246.1	475.0	229.4	445.0	213.0	415.4
246.0	474.8	229.0	444.2	212.8	415.0
245.5	474.0	228.9	444.0	212.2	414.0
245.0	473.0	228.3	443.0	212.0	413.6
244.4	472.0	228.0	442.4	211.6	413.0
244.0	471.2	227.8	442.0	211.1	412.0
243.9	471.0	227.2	441.0	211.0	411.8
243.3	470.0	227.0	440.6	210.5	411.0
243.0	469.4	226.6	440.0	210.0	410.0
242.8	469.0	226.1	439.0	209.4	409.0
242.2	468.0	226.0	438.8	209.0	408.2
242.0	467.6	225.5	438.0	208.9	408.0
241.6	467.0	225.0	437.0	208.3	407.0
241.1	466.0	224.4	436.0	208.0	406.4
241.0	465.8	224.0	435.2	207.8	406.0
240.5	465.0	223.9	435.0	207.2	405.0
240.0	464.0	223.3	434.0	207.0	404.6
239.4	463.0	223.0	433.4	206.6	404.0
239.0	462.2	222.8	433.0	206.1	403.0
238.9	462.0	222.2	432.0	206.0	402.8
238.3	461.0	222.0	431.6	205.5	402.0
238.0	460.4	221.6	431.0	205.0	401.0
237.8	460.0	221.1	430.0	204.4	400.0
237.2	459.0	221.0	429.8	204.0	399.2
237.0	458.6	220.5	429.0	203.9	399.0

C.	F.	C.	F.	C.	F.
203.3	398.0	187.0	368.6	170.5	339.0
203.0	397.4	186.6	368.0	170.0	338.0
202.8	397.0	186.1	367.0	169.4	337.0
202.2	396.0	186.0	366.8	169.0	336.2
202.0	395.6	185.5	366.0	168.9	336.0
201.6	395.0	185.0	365.0	168.3	335.0
201.1	394.0	184.4	364.0	168.0	334.4
201.0	393.8	184.0	363.2	167.8	334.0
200.5	393.0	183.9	363.0	167.2	333.0
200.0	392.0	183.3	362.0	167.0	332.6
199.4	391.0	183.0	361.4	166.6	332.0
199.0	390.2	182.8	361.0	166.1	331.0
198.9	390.0	182.2	360.0	166.0	330.8
198.3	389.0	182.0	359.6	165.5	330.0
198.0	388.4	181.6	359.0	165.0	329.0
197.8	388.0	181.1	358.0	164.4	328.0
197.2	387.0	181.0	357.8	164.0	327.2
197.0	386.6	180.5	357.0	163.9	327.0
196.6	386.0	180.0	356.0	163.3	326.0
196.1	385.0	179.4	355.0	163.0	325.4
196.0	384.8	179.0	354.2	162.8	325.0
195.5	384.0	178.9	354.0	162.2	324.0
195.0	383.0	178.3	353.0	162.0	323.6
194.4	382.0	178.0	352.4	161.6	323.0
194.0	381.2	177.8	352.0	161.1	322.0
193.9	381.0	177.2	351.0	161.0	321.8
193.3	380.0	177.0	350.6	160.5	321.0
193.0	379.4	176.6	350.0	160.0	320.0
192.8	379.0	176.1	349.0	159.4	319.0
192.2	378.0	176.0	348.8	159.0	318.2
192.0	377.6	175.5	348.0	158.9	318.0
191.6	377.0	175.0	347.0	158.3	317.0
191.1	376.0	174.4	346.0	158.0	316.4
191.0	375.8	174.0	345.2	157.8	316.0
190.5	375.0	173.9	345.0	157.2	315.0
190.0	374.0	173.3	344.0	157.0	314.6
189.4	373.0	173.0	343.4	156.6	314.0
189.0	372.2	172.8	343.0	156.1	313.0
188.9	372.0	172.2	342.0	156.0	312.8
188.3	371.0	172.0	341.6	155.5	312.0
188.0	370.4	171.6	341.0	155.0	311.0
187.8	370.0	171.1	340.0	154.4	310.0
187.2	369.0	171.0	339.8	154.0	309.2

C.	F.	C.	F.	C.	F.
153.9	309.0	137.2	279.0	121.0	249.8
153.3	308.0	137.0	278.6	120.5	249.0
153.0	307.4	136.6	278.0	120.0	248.0
152.8	307.0	136.1	277.0	119.4	247.0
152.2	306.0	136.0	276.8	119.0	246.2
152.0	305.6	135.5	276.0	118.9	246.0
151.6	305.0	135.0	275.0	118.3	245.0
151.1	304.0	134.4	274.0	118.0 ·	244.4
151.0	303.8	134.0	273.2	117.8	244.0
150.5	303.0	133.9	273.0	117.2	243.0
150.0	302.0	133.3	272.0	117.0	242.6
149.4	301.0	133.0	271.4	116.6	242.0
149.0	300.2	132.8	271.0	116.1	241.0
148.9	300.0	132.2	270.0	116.0	240.8
148.3	299.0	132.0	269.6	115.5	240.0
148.0	298.4	131.6	269.0	115.0	239.0
147.8	298.0	131.1	268.0	114.4	238.0
147.2	297.0	131.0	267.8	114.0	237.2
147.0	296.6	130.5	267.0	113.9	237.0
146.6	296.0	130.0	266.0	113.3	236.0
146.1	295.0	129.4	265.0	113.0	235.4
146.0	294.8	129.0	264.2	112.8	235.0
145.5	294.0	128.9	264.0	112.2	234.0
145.0	293.0	128.3	263.0	112.0	233.6
144.4	292.0	128.0	262.4	111.6	233.0
144.0	291.2	127.8	262.0	111.1	232.0
143.9	291.0	127.2	261.0	111.0 ·	231.8
143.3	290.0	127.0	260.6	110.5	231.0
143.0	289.4	126.6	260.0	110.0	230.0
142.8	289.0	126.1	259.0	109.4	229.0
142.2	288.0	126.0	258.8	109.0 .	228.2
142.0	287.6	125.5	258.0	108.9	228.0
141.6	287.0	125.0	257.0	108.3	227.0
141.1	286.0	124.4	256.0	108.0	226.4
141.0	285.8	124.0	255.2	107.8	226.0
140.5	285.0	123.9	255.0	107.2	225.0
140.0	284.0	123.3	254.0	107.0	224.6
139.4	283.0	123.0	253.4	106.6	224.0
139.0	282.2	122.8	253.0	106.1	223.0
138.9	282.0	122.2	252.0	106.0	222.8
138.3	281.0	122.0	251.6	105.5	222.0
138.0	280.4	121.6	251.0	105.0	221.0
137.8	280.0	121.1	250.0	104.4	220.0

C.	F.	C.	F.	C.	F.
104.0	219.2	87.8	190.0	71.1	160.0
103.9	219.0	87.2	189.0	71.0	159.8
103.3	218.0	87.0	188.6	70.5	159.0
103.0	217.4	86.6	188.0	70.0	158.0
102.8	217.0	86.1	187.0	69.4	157.0
102.2	216.0	86.0	186.8	69.0	156.2
102.0	215.6	85.5	186.0	68.9	156.0
101.6	215.0	85.0	185.0	68.3	155.0
101.1	214.0	84.4	184.0	68.0	154.4
101.0	213.8	84.0	183.2	67.8	154.0
100.5	213.0	83.9	183.0	67.2	153.0
100.0	**212.0**	83.3	182.0	67.0	152.6
99.4	211.0	83.0	181.4	66.6	152.0
99.0	210.2	82.8	181.0	66.1	151.0
98.9	210.0	82.2	180.0	66.0	150.8
98.3	209.0	82.0	179.6	65.5	150.0
98.0	208.4	81.6	179.0	65.0	149.0
97.8	208.0	81.1	178.0	64.4	148.0
97.2	207.0	81.0	177.8	64.0	147.2
97.0	206.6	80.5	177.0	63.9	147.0
96.6	206.0	80.0	176.0	63.3	146.0
96.1	205.0	79.4	175.0	63.0	145.4
96.0	204.8	79.0	174.2	62.8	145.0
95.5	204.0	78.9	174.0	62.2	144.0
95.0	203.0	78.3	173.0	62.0	143.6
94.4	202.0	78.0	172.4	61.6	143.0
94.0	201.2	77.8	172.0	61.1	142.0
93.9	201.0	77.2	171.0	61.0	141.8
93.3	200.0	77.0	170.6	60.5	141.0
93.0	199.4	76.6	170.0	60.0	140.0
92.8	199.0	76.1	169.0	59.4	139.0
92.2	198.0	76.0	168.8	59.0	138.2
92.0	197.6	75.5	168.0	58.9	138.0
91.6	197.0	75.0	167.0	58.3	137.0
91.1	196.0	74.4	166.0	58.0	136.4
91.0	195.8	74.0	165.2	57.8	136.0
90.5	195.0	73.9	165.0	57.2	135.0
90.0	194.0	73.3	164.0	57.0	134.6
89.4	193.0	73.0	163.4	56.6	134.0
89.0	192.2	72.8	163.0	56.1	133.0
88.9	192.0	72.2	162.0	56.0	132.8
88.3	191.0	72.0	161.6	55.5	132.0
88.0	190.4	71.6	161.0	55.0	131.0

C.	F.	C.	F.	C.	F.
54.4	130.0	38.0	100.4	21.6	71.0
54.0	129.2	37.8	100.0	21.1	70.0
53.9	129.0	37.2	99.0	21.0	69.8
53.3	128.0	**37.0**	**98.6**	20.6	69.0
53.0	127.4	36.6	98.0	20.0	68.0
52.8	127.0	36.1	97.0	19.4	67.0
52.2	126.0	36.0	96.8	19.0	66.2
52.0	125.6	35.5	96.0	18.9	66.0
51.6	125.0	35.0	95.0	18.4	65.0
51.1	124.0	34.4	94.0	18.0	64.4
51.0	123.8	34.0	93.2	17.7	64.0
50.5	123.0	33.9	93.0	17.2	63.0
50.0	122.0	33.3	92.0	17.0	62.6
49.4	121.0	33.0	91.4	16.6	62.0
49.0	120.2	32.8	91.0	16.1	61.0
48.9	120.0	32.2	90.0	16.0	60.8
48.3	119.0	32.0	89.6	**15.55**	**60.0**
48.0	118.4	31.6	89.0	15.0	59.0
47.8	118.0	31.1	88.0	14.4	58.0
47.2	117.0	31.0	87.8	14.0	57.2
47.0	116.6	30.5	87.0	13.9	57.0
46.6	116.0	30.0	86.0	13.3	56.0
46.1	115.0	29.6	85.0	13.0	55.4
46.0	114.8	29.0	84.2	12.7	55.0
45.5	114.0	28.9	84.0	12.2	54.0
45.0	113.0	28.3	83.0	12.0	53.6
44.4	112.0	28.0	82.4	11.6	53.0
44.0	111.2	27.9	82.0	11.1	52.0
43.9	111.0	27.3	81.0	11.0	51.8
43.3	110.0	27.0	80.6	10.6	51.0
43.0	109.4	26.7	80.0	10.0	50.0
42.8	109.0	26.2	79.0	9.4	49.0
42.2	108.0	26.0	78.8	9.0	48.2
42.0	107.6	25.6	78.0	8.9	48.0
41.6	107.0	25.0	77.0	8.3	47.0
41.1	106.0	24.4	76.0	8.0	46.4
41.0	105.8	24.0	75.2	7.7	46.0
40.5	105.0	23.9	75.0	7.2	45.0
40.0	104.0	23.3	74.0	7.0	44.6
39.4	103.0	23.0	73.4	6.6	44.0
39.0	102.2	22.7	73.0	6.1	43.0
38.9	102.0	22.2	72.0	6.0	42.8
38.3	101.0	22.0	71.6	5.6	42.0

C.	F.	C.	F.	C.	F.
5.0	41.0	−11.6	11.0	−28.0	−18.4
4.4	40.0	−12.0	10.4	−28.3	−19.0
4.0	**39.2**	−12.2	10.0	−28.9	−20.0
3.9	39.0	−12.7	9.0	−29.0	−20.2
3.3	38.0	−13.0	8.6	−29.4	−21.0
3.0	37.4	−13.3	8.0	−30.0	−22.0
2.7	37.0	−13.9	7.0	−30.5	−23.0
2.2	36.0	−14.0	6.8	−31.0	−23.8
2.0	35.6	−14.4	6.0	−31.1	−24.0
1.6	35.0	−15.0	5.0	−31.6	−25.0
1.1	34.0	−15.5	4.0	−32.0	−25.6
1.0	33.8	−16.0	3.2	−32.2	−26.0
0.6	33.0	−16.1	3.0	−32.7	−27.0
0.0	**32.0**	−16.6	2.0	−33.0	−27.4
−0.5	31.0	−17.0	1.4	−33.3	−28.0
−1.0	30.2	−17.2	1.0	−33.9	−29.0
−1.1	30.0	**−17.7**	**0.0**	−34.0	−29.2
−1.6	29.0	−18.0	−0.4	−34.4	−30.0
−2.0	28.4	−18.3	−1.0	−35.0	−31.0
−2.2	28.0	−18.8	−2.0	−35.5	−32.0
−2.7	27.0	−19.0	−2.2	−36.0	−32.8
−3.0	26.6	−19.4	−3.0	−36.1	−33.0
−3.3	26.0	−20.0	−4.0	−36.6	−34.0
−3.9	25.0	−20.5	−5.0	−37.0	−34.6
−4.0	24.8	−21.0	−5.8	−37.2	−35.0
−4.4	24.0	−21.1	−6.0	−37.7	−36.0
−5.0	23.0	−21.6	−7.0	−38.0	−36.4
−5.5	22.0	−22.0	−7.6	−38.3	−37.0
−6.0	21.2	−22.2	−8.0	−38.9	−38.0
−6.1	21.0	−22.7	−9.0	−39.0	−38.2
−6.6	20.0	−23.0	−9.4	−39.4	−39.0
−7.0	19.4	−23.3	−10.0	**−40.0**	**−40.0**
−7.2	19.0	−23.9	−11.0	−40.5	−41.0
−7.7	18.0	−24.0	−11.2	−41.0	−41.8
−8.0	17.6	−24.4	−12.0	−41.1	−42.0
−8.3	17.0	−25.0	−13.0	−41.6	−43.0
−8.9	16.0	−25.5	−14.0	−42.0	−43.6
−9.0	15.8	−26.0	−14.8	−42.2	−44.0
−9.4	15.0	−26.1	−15.0	−42.7	−45.0
−10.0	14.0	−26.6	−16.0	−43.0	−45.4
−10.5	13.0	−27.0	−16.6	−43.3	−46.0
−11.0	12.2	−27.2	−17.0	−43.8	−47.0
−11.1	12.0	−27.7	−18.0	−44.0	−47.2

C.	F.	C.	F.	C.	F.
−44.4	−48.0	−61.1	−78.0	−77.7	−108.0
−45.0	−49.0	−61.6	−79.0	−78.0	−108.4
−45.5	−50.0	−62.0	−79.6	−78.3	−109.0
−46.0	−50.8	−62.2	−80.0	−78.8	−110.0
−46.1	−51.0	−62.7	−81.0	−79.0	−110.2
−46.6	−52.0	−63.0	−81.4	−79.4	−111.0
−47.0	−52.6	−63.3	−82.0	−80.0	−112.0
−47.2	−53.0	−63.8	−83.0	−80.5	−113.0
−47.7	−54.0	−64.0	−83.2	−81.0	−113.8
−48.0	−54.4	−64.4	−84.0	−81.1	−114.0
−48.3	−55.0	−65.0	−85.0	−81.6	−115.0
−48.8	−56.0	−65.5	−86.0	−82.0	−115.6
−49.0	−56.2	−66.0	−86.8	−82.2	−116.0
−49.4	−57.0	−66.1	−87.0	−82.7	−117.0
−50.0	−58.0	−66.6	−88.0	−83.0	−117.4
−50.5	−59.0	−67.0	−88.6	−83.3	−118.0
−51.0	−59.8	−67.2	−89.0	−83.8	−119.0
−51.1	−60.0	−67.7	−90.0	−84.0	−119.2
−51.6	−61.0	−68.0	−90.4	−84.4	−120.0
−52.0	−61.6	−68.3	−91.0	−85.0	−121.0
−52.2	−62.0	−68.8	−92.0	−85.5	−122.0
−52.7	−63.0	−69.0	−92.2	−86.0	−122.8
−53.0	−63.4	−69.4	−93.0	−86.1	−123.0
−53.3	−64.0	−70.0	−94.0	−86.6	−124.0
−53.8	−65.0	−70.5	−95.0	−87.0	−124.6
−54.0	−65.2	−71.0	−95.8	−87.2	−125.0
−54.4	−66.0	−71.1	−96.0	−87.7	−126.0
−55.0	−67.0	−71.6	−97.0	−88.0	−126.4
−55.5	−68.0	−72.0	−97.6	−88.3	−127.0
−56.0	−68.8	−72.2	−98.0	−88.8	−128.0
−56.1	−69.0	−72.7	−99.0	−89.0	−128.2
−56.6	−70.0	−73.0	−99.4	−89.4	−129.0
−57.0	−70.6	−73.3	−100.0	−90.0	−130.0
−57.2	−71.0	−73.8	−101.0	−90.5	−131.0
−57.7	−72.0	−74.0	−101.2	−91.0	−131.8
−58.0	−72.4	−74.4	−102.0	−91.1	−132.0
−58.3	−73.0	−75.0	−103.0	−91.6	−133.0
−58.8	−74.0	−75.5	−104.0	−92.0	−133.6
−59.0	−74.2	−76.0	−104.8	−92.2	−134.0
−59.4	−75.0	−76.1	−105.0	−92.7	−135.0
−60.0	−76.0	−76.6	−106.0	−93.0	−135.4
−60.5	−77.0	−77.0	−106.6	−93.3	−136.0
−61.0	−77.8	−77.2	−107.0	−93.8	−137.0

C.	F.	C.	F.	C.	F.
−94.0	−137.2	−111.0	−167.8	−127.2	−197.0
−94.4	−138.0	−111.1	−168.0	−127.7	−198.0
−95.0	−139.0	−111.6	−169.0	−128.0	−198.4
−95.5	−140.0	−112.0	−169.6	−128.3	−199.0
−96.0	−140.8	−112.2	−170.0	−128.8	−200.0
−96.1	−141.0	−112.7	−171.0	−129.0	−200.2
−96.6	−142.0	−113.0	−171.4	−129.4	−201.0
−97.0	−142.6	−113.3	−172.0	−130.0	−202.0
−97.2	−143.0	−113.8	−173.0	−130.5	−203.0
−97.7	−144.0	−114.0	−173.2	−131.0	−203.8
−98.0	−144.4	−114.4	−174.0	−131.1	−204.0
−98.3	−145.0	−115.0	−175.0	−131.6	−205.0
−98.8	−146.0	−115.5	−176.0	−132.0	−205.6
−99.0	−146.2	−116.0	−176.8	−132.2	−206.0
−99.4	−147.0	−116.1	−177.0	−132.7	−207.0
−100.0	−148.0	−116.6	−178.0	−133.0	−207.4
−100.5	−149.0	−117.0	−178.6	−133.3	−208.0
−101.0	−149.8	−117.2	−179.0	−133.8	−209.0
−101.1	−150.0	−117.7	−180.0	−134.0	−209.2
−101.6	−151.0	−118.0	−180.4	−134.4	−210.0
−102.0	−151.6	−118.3	−181.0	−135.0	−211.0
−102.2	−152.0	−118.8	−182.0	−135.5	−212.0
−102.7	−153.0	−119.0	−182.2	−136.0	−212.8
−103.0	−153.4	−119.4	−183.0	−136.1	−213.0
−103.3	−154.0	−120.0	−184.0	−136.6	−214.0
−103.8	−155.0	−120.5	−185.0	−137.0	−214.6
−104.0	−155.2	−121.0	−185.8	−137.2	−215.0
−104.4	−156.0	−121.1	−186.0	−137.7	−216.0
−105.0	−157.0	−121.6	−187.0	−138.0	−216.4
−105.5	−158.0	−122.0	−187.6	−138.3	−217.0
−106.0	−158.8	−122.2	−188.0	−138.8	−218.0
−106.1	−159.0	−122.7	−189.0	−139.0	−218.2
−106.6	−160.0	−123.0	−189.4	−139.4	−219.0
−107.0	−160.6	−123.3	−190.0	−140.0	−220.0
−107.2	−161.0	−123.8	−191.0	−140.5	−221.0
−107.7	−162.0	−124.0	−191.2	−141.0	−221.8
−108.0	−162.4	−124.4	−192.0	−141.1	−222.0
−108.3	−163.0	−125.0	−193.0	−141.6	−223.0
−108.8	−164.0	−125.5	−194.0	−142.0	−223.6
−109.0	−164.2	−126.0	−194.8	−142.2	−224.0
−109.4	−165.0	−126.1	−195.0	−142.7	−225.0
−110.0	−166.0	−126.6	−196.0	−143.0	−225.4
−110.5	−167.0	−127.0	−196.6	−143.3	−226.0

C.	F.	C.	F.	C.	F.
—143.8	—227.0	—149.0	—236.2	—154.4	—246.0
—144.0	—227.2	—149.4	—237.2	—155.0	—247.0
—144.4	—228.0	—150.0	—238.0	—155.5	—248.0
—145.0	—229.0	—150.5	—239.0	—156.0	—248.8
—145.5	—230.0	—151.0	—239.8	—156.1	—249.0
—146.0	—230.8	—151.1	—240.0	—156.6	—250.0
—146.1	—231.0	—151.6	—241.0	—157.0	—250.6
—146.6	—232.0	—152.0	—241.6	—157.2	—251.0
—147.0	—232.6	—152.2	—242.0	—157.7	—252.0
—147.2	—233.0	—152.7	—243.0	—158.0	—252.4
—147.7	—234.0	—153.0	—243.4	—158.3	—253.0
—148.0	—234.4	—153.3	—244.0	—158.8	—254.0
—148.3	—235.0	—153.8	—245.0	—159.0	—254.2
—148.8	—236.0	—154.0	—245.2	—159.4	—255.0

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